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(54) **AROMATIC HETEROCYCLIC-BASED
CHARGE TRANSPORT MATERIALS
HAVING TWO AMINO GROUPS**

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430/77, 79; 399/159
See application file for complete search history.

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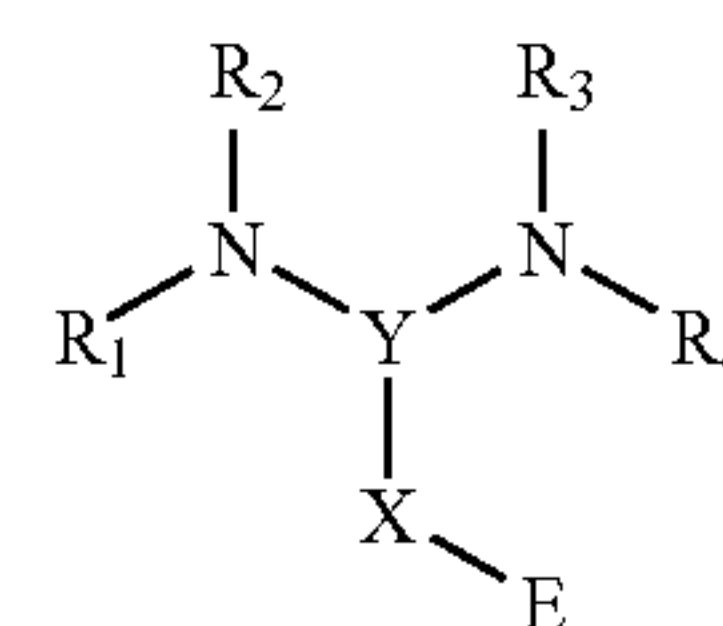
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(57) **ABSTRACT**

Improved organophotoreceptor comprises an electrically
conductive substrate and a photoconductive element on the
electrically conductive substrate, the photoconductive ele-
ment comprising:

(a) a charge transport material having the formula



where Y comprises an aromatic heterocyclic group;

X is a bond or a linking group;

E comprises a reactive ring group or a reactive functional
group; and

R₁, R₂, R₃, and R₄ comprise, each independently, H, an
alkyl group, an acyl group, an ether group, an alkenyl
group, an alkynyl group, a heterocyclic group, an
aromatic group, or a part of a ring group; and

(b) a charge generating compound.

Corresponding electrophotographic apparatuses, electro-
photographic imaging methods, and bridged charge trans-
port materials derived from the charge transport material
above are also described.

32 Claims, No Drawings

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AROMATIC HETEROCYCLIC-BASED CHARGE TRANSPORT MATERIALS HAVING TWO AMINO GROUPS

FIELD OF THE INVENTION

This invention relates to organophotoreceptors suitable for use in electrophotography and, more specifically, to organophotoreceptors including a charge transport material having a diamino-aromatic heterocyclic group bonded to a reactive group directly or through a linking group. The invention also relates to a bridged charge transport material derived from the reaction of the diamino-aromatic heterocyclic charge transport material with a bridging compound.

BACKGROUND OF THE INVENTION

In electrophotography, an organophotoreceptor in the form of a plate, disk, sheet, belt, drum or the like having an electrically insulating photoconductive element on an electrically conductive substrate is imaged by first uniformly electrostatically charging the surface of the photoconductive layer, and then exposing the charged surface to a pattern of light. The light exposure selectively dissipates the charge in the illuminated areas where light strikes the surface, thereby forming a pattern of charged and uncharged areas, referred to as a latent image. A liquid or solid toner is then provided in the vicinity of the latent image, and toner droplets or particles deposit in the vicinity of either the charged or uncharged areas to create a toned image on the surface of the photoconductive layer. The resulting toned image can be transferred to a suitable ultimate or intermediate receiving surface, such as paper, or the photoconductive layer can operate as an ultimate receptor for the image. The imaging process can be repeated many times to complete a single image, for example, by overlaying images of distinct color components or effect shadow images, such as overlaying images of distinct colors to form a full color final image, and/or to reproduce additional images.

Both single layer and multilayer photoconductive elements have been used. In single layer embodiments, a charge transport material and charge generating material are combined with a polymeric binder and then deposited on the electrically conductive substrate. In multilayer embodiments, the charge transport material and charge generating material are present in the element in separate layers, each of which can optionally be combined with a polymeric binder, deposited on the electrically conductive substrate. Two arrangements are possible for a two-layer photoconductive element. In one two-layer arrangement (the "dual layer" arrangement), the charge-generating layer is deposited on the electrically conductive substrate and the charge transport layer is deposited on top of the charge generating layer. In an alternate two-layer arrangement (the "inverted dual layer" arrangement), the order of the charge transport layer and charge generating layer is reversed.

In both the single and multilayer photoconductive elements, the purpose of the charge generating material is to generate charge carriers (i.e., holes and/or electrons) upon exposure to light. The purpose of the charge transport material is to accept at least one type of these charge carriers and transport them through the charge transport layer in order to facilitate discharge of a surface charge on the photoconductive element. The charge transport material can be a charge transport compound, an electron transport compound, or a combination of both. When a charge transport compound is used, the charge transport compound accepts

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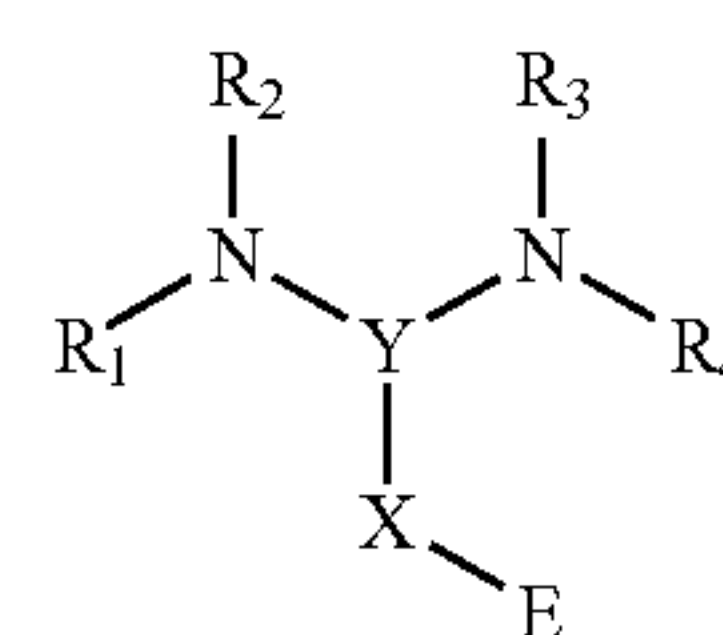
the hole carriers and transports them through the layer with the charge transport compound. When an electron transport compound is used, the electron transport compound accepts the electron carriers and transports them through the layer with the electron transport compound.

SUMMARY OF THE INVENTION

This invention provides organophotoreceptors having good electrostatic properties such as high V_{acc} and low V_{dis} .

In a first aspect, an organophotoreceptor comprises an electrically conductive substrate and a photoconductive element on the electrically conductive substrate, the photoconductive element comprising:

(a) a charge transport material having the formula:



(I)

where Y comprises an aromatic heterocyclic group;

X is a bond or a linking group, such as a $-(CH_2)_m-$ group, where m is an integer between 1 and 20, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group, a BR_g group, or a $P(=O)R_h$ group, where R_a , R_b , R_c , R_d , R_e , R_f , R_g , and R_h are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an acyl group, an alkoxy group, an alkylsulfanyl group, an alkenyl group, such as a vinyl group, an allyl group, and a 2-phenylethenyl group, an alkynyl group, a heterocyclic group, an aromatic group, a part of a ring group, such as cycloalkyl groups, heterocyclic groups, and a benzo group, or an alkyl group where one or more of the hydrogens of the alkyl group is optionally replaced by an aromatic group, a hydroxyl group, a thiol group, a carboxyl group, an amino group, or a halogen;

E comprises a reactive ring group, such as an epoxy group, a thiiranyl group, an aziridiny group, and an oxetanyl group, a reactive functional group, such as a hydroxyl group, a thiol group, a carboxyl group, and an amino group, or an ethylenically unsaturated group, such as a vinyl ether group, an alkene group, acrylate group, a methacrylate group, an acrylamide group, and a methacrylamide group; and

R_1 , R_2 , R_3 , and R_4 comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group such as cycloalkyl groups, heterocyclic groups, and a benzo group; and

(b) a charge generating compound.

The organophotoreceptor may be provided, for example, in the form of a plate, a flexible belt, a flexible disk, a sheet, a rigid drum, or a sheet around a rigid or compliant drum. In one embodiment, the organophotoreceptor includes: (a) a photoconductive element comprising the charge transport material, the charge generating compound, a second charge transport material, and a polymeric binder; and (b) the electrically conductive substrate.

In a second aspect, the invention features an electrophotographic imaging apparatus that comprises (a) a light

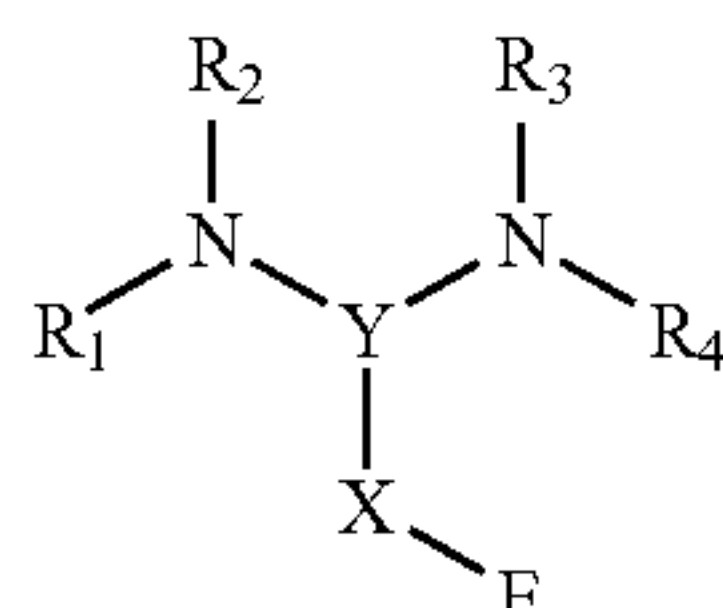
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imaging component; and (b) the above-described organophotoreceptor oriented to receive light from the light imaging component. The apparatus can further comprise a toner dispenser, such as a liquid toner dispenser. The method of electrophotographic imaging with photoreceptors containing the above noted charge transport materials is also described.

In a third aspect, the invention features an electrophotographic imaging process that includes (a) applying an electrical charge to a surface of the above-described organophotoreceptor; (b) imagewise exposing the surface of the organophotoreceptor to radiation to dissipate charge in selected areas and thereby form a pattern of at least relatively charged and uncharged areas on the surface; (c) contacting the surface with a toner, such as a liquid toner that includes a dispersion of colorant particles in an organic liquid, to create a toned image; and (d) transferring the toned image to a substrate.

In a fourth aspect, the invention features a charge transport material having Formula (I) above.

In a fifth aspect, the invention features a method of preparing a bridged charge transport material by reacting a bridging compound having a formula HQ_1-Z-Q_2H with at least a compound having a reactive ring group comprising the following formula:



where Y comprises an aromatic heterocyclic group;

X and Z are, each independently, a bond or a linking group, such as a $-(CH_2)_m-$ group, where m is an integer between 1 and 20, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group, a BR_g group, or a $P(=O)R_h$ group, where $R_a, R_b, R_c, R_d, R_e, R_f, R_g,$ and R_h are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, an acyl group, an alkoxy group, an alkylsulfanyl group, an alkenyl group, such as a vinyl group, an allyl group, and a 2-phenylethenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as cycloalkyl groups, heterocyclic groups, and a benzo group;

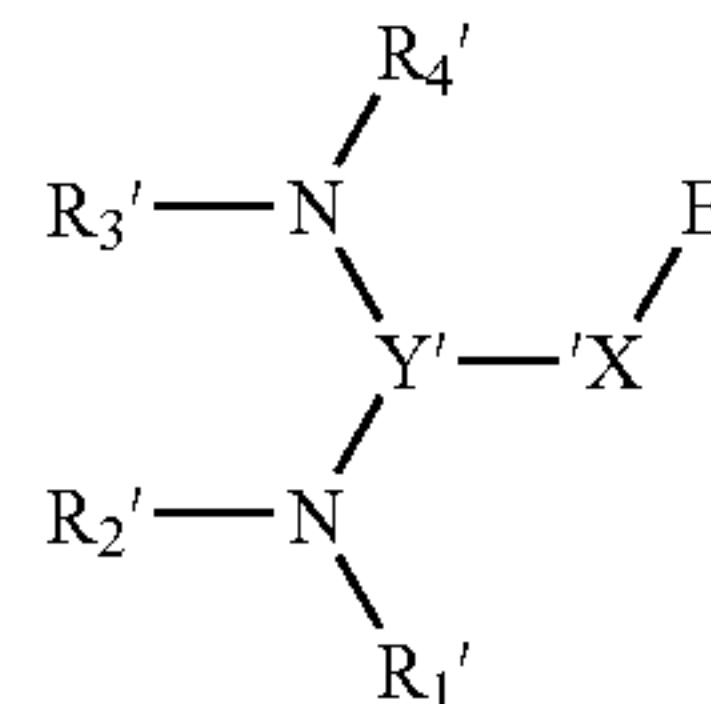
E comprises a reactive ring group, such as an epoxy group, a thiiranyl group, an aziridinyl group, and an oxetanyl group, a reactive functional group, such as a hydroxyl group, a thiol group, a carboxyl group, and an amino group, or an ethylenically unsaturated group, such as a vinyl ether group, an alkene group, acrylate group, a methacrylate group, an acrylamide group, and a methacrylamide group;

Q_1 and Q_2 are each independently, O, S, and NR; and

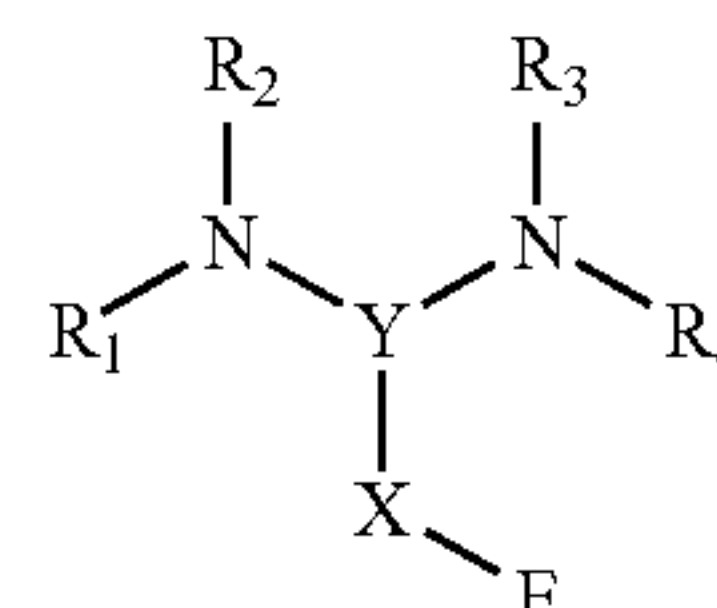
$R, R_1, R_2, R_3,$ and R_4 comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group such as cycloalkyl groups, heterocyclic groups, and a benzo group.

In a sixth aspect, the invention features a method of preparing a bridged charge transport material by reacting a reactive functional compound having the following formula:

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with a reactive ring compound having the following formula:



where Y and Y', each independently, comprise an aromatic heterocyclic group;

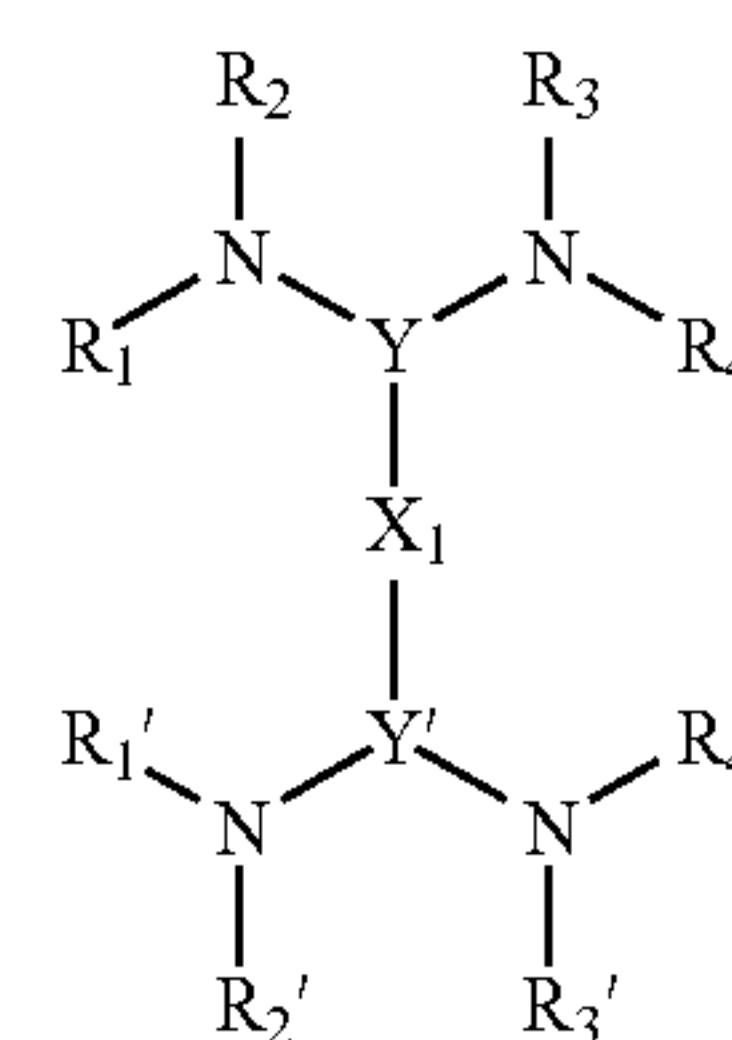
X and X' comprise, each independently, a bond or a linking group;

E comprises a reactive ring group;

E' comprises a reactive functional group;

$R_1', R_2', R_3', R_4', R_1, R_2, R_3,$ and R_4 comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group.

In a seventh aspect, the invention features a bridged charge transport material having the formula:



where Y and Y', each independently, comprise an aromatic heterocyclic group;

X_1 is a first linking group, such as a $-(CH_2)_m-$ group, where m is an integer between 1 and 66, inclusive, and one of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group, a BR_g group, or a $P(=O)R_h$ group, where $R_a, R_b, R_c, R_d, R_e, R_f, R_g,$ and R_h are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, an acyl group, an alkoxy group, an alkylsulfanyl group, an alkenyl group, such as a vinyl group, an allyl group, and a 2-phenylethenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as cycloalkyl groups, heterocyclic groups, and a benzo group; and

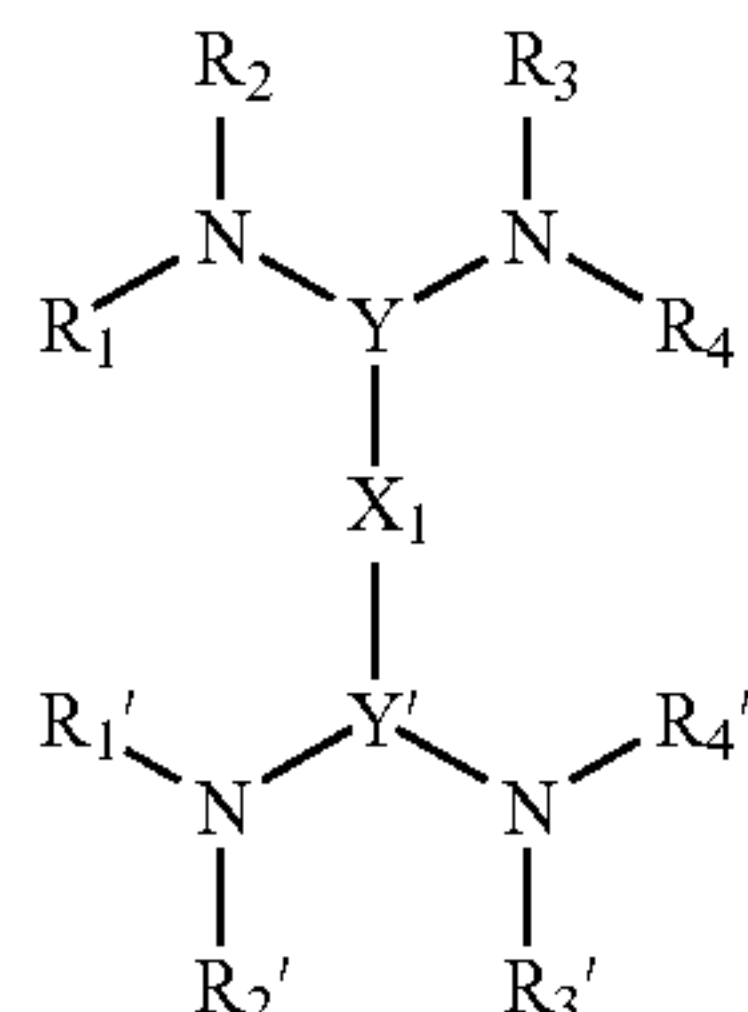
$R_1, R_2, R_3, R_4, R_1', R_2', R_3',$ and R_4' comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic

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group, an aromatic group, or a part of a ring group such as cycloalkyl groups, heterocyclic groups, and a benzo group.

In an eighth aspect, the invention features an organophotoreceptor comprising an electrically conductive substrate and a photoconductive element on the electrically conductive substrate, the photoconductive element comprising:

(a) a bridged charge transport material having the formula



where Y and Y', each independently, comprise an aromatic heterocyclic group;

X₁ is a first linking group; and

R₁, R₂, R₃, R₄, R₁', R₂', R₃', and R₄' comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group; and

(b) a charge generating compound.

The invention provides suitable charge transport materials for organophotoreceptors featuring a combination of good mechanical and electrostatic properties. These photoreceptors can be used successfully with toners, such as liquid toners, to produce high quality images. The high quality of the imaging system can be maintained after repeated cycling.

Other features and advantages of the invention will be apparent from the following description of the particular embodiments thereof, and from the claims.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

An organophotoreceptor as described herein has an electrically conductive substrate and a photoconductive element including a charge generating compound and a charge transport material having a diamino-aromatic heterocyclic group bonded to a reactive group directly or through a linking group. The charge transport material may also be a dimeric charge transport material derived from the reaction of a bridging compound with the charge transport material having a diamino-aromatic heterocyclic group bonded to a functional group directly or through a linking group. These charge transport materials have desirable properties as evidenced by their performance in organophotoreceptors for electrophotography. In particular, the charge transport materials of this invention have high charge carrier mobilities and good compatibility with various binder materials, and possess excellent electrophotographic properties. The organophotoreceptors according to this invention generally have a high photosensitivity, a low residual potential, and a high stability with respect to cycle testing, crystallization, and organophotoreceptor bending and stretching. The organophotoreceptors are particularly useful in laser printers and the like as well as fax machines, photocopiers, scanners and other electronic devices based on electrophotography. The use of these charge transport materials is described in more detail below in the context of laser printer use, although their

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application in other devices operating by electrophotography can be generalized from the discussion below.

To produce high quality images, particularly after multiple cycles, it is desirable for the charge transport materials to form a homogeneous solution with the polymeric binder and remain approximately homogeneously distributed through the organophotoreceptor material during the cycling of the material. In addition, it is desirable to increase the amount of charge that the charge transport material can accept (indicated by a parameter known as the acceptance voltage or "V_{acc}"), and to reduce retention of that charge upon discharge (indicated by a parameter known as the discharge voltage or "V_{dis}").

The charge transport materials may comprise monomeric molecules (e.g., 9-ethyl-carbazole-3-carbaldehyde N,N-diphenylhydrazone), dimeric molecules (e.g., those disclosed in U.S. Pat. Nos. 6,140,004, 6,670,085, and 6,749,978), or polymeric compositions (e.g., poly(vinylcarbazole)). The charge transport materials can also be classified as a charge transport compound or an electron transport compound. There are many charge transport compounds and electron transport compounds known in the art for electrophotography. Non-limiting examples of charge transport compounds include, for example, pyrazoline derivatives, fluorene derivatives, oxadiazole derivatives, stilbene derivatives, enamine derivatives, enamine stilbene derivatives, hydrazone derivatives, carbazole hydrazone derivatives, (N,N-disubstituted)arylamines such as triaryl amines, polyvinyl carbazole, polyvinyl pyrene, polyacacenaphthylene, and the charge transport compounds described in U.S. Pat. Nos. 6,670,085, 6,689,523, 6,696,209, and 6,749,978, and U.S. patent application Ser. Nos. 10/431,135, 10/431,138, 10/699,364, 10/663,278, 10/699,581, 10/449,554, 10/748,496, 10/789,094, 10/644,547, 10/749,174, 10/749,171, 10/749,418, 10/699,039, 10/695,581, 10/692,389, 10/634,164, 10/663,970, 10/749,164, 10/772,068, 10/749,178, 10/758,869, 10/695,044, 10/772,069, 10/789,184, 10/789,077, 10/775,429, 10/775,429, 10/670,483, 10/671,255, 10/663,971, 10/760,039. All the above patents and patent applications are incorporated herein by reference.

Non-limiting examples of electron transport compounds include, for example, bromoaniline, tetracyanoethylene, tetracyanoquinodimethane, 2,4,7-trinitro-9-fluorenone, 2,4,5,7-tetranitro-9-fluorenone, 2,4,5,7-tetranitroxanthone, 2,4,8-trinitrothioxanthone, 2,6,8-trinitro-indeno[1,2-b]thiophene-4-one, and 1,3,7-trinitrodibenzo thiophene-5,5-dioxide, (2,3-diphenyl-1-indenylidene)malononitrile, 4H-thiopyran-1,1-dioxide and its derivatives such as 4-dicyanomethylene-2,6-diphenyl-4H-thiopyran-1,1-dioxide, 4-dicyanomethylene-2,6-di-m-tolyl-4H-thiopyran-1,1-dioxide, and unsymmetrically substituted 2,6-diaryl-4H-thiopyran-1,1-dioxide such as 4H-1,1-dioxo-2-(p-isopropylphenyl)-6-phenyl-4-(dicyanomethylidene)thiopyran and 4H-1,1-dioxo-2-(p-isopropylphenyl)-6-(2-thienyl)-4-(dicyanomethylidene)thiopyran, derivatives of phospho-2,5-cyclohexadiene, alkoxycarbonyl-9-fluorenylidene)malononitrile derivatives such as (4-n-butoxycarbonyl-9-fluorenylidene)malononitrile, (4-phenethoxycarbonyl-9-fluorenylidene)malononitrile, (4-carbitoxy-9-fluorenylidene)malononitrile, and diethyl(4-n-butoxycarbonyl-2,7-dinitro-9-fluorenylidene)malonate, anthraquinodimethane derivatives such as 11,11,12,12-tetracyano-2-alkylanthraquinodimethane and 11,11-dicyano-12,12-bis(ethoxycarbonyl)anthraquinodimethane, anthrone derivatives such as 1-chloro-10-[bis(ethoxycarbonyl)methylene]anthrone, 1,8-dichloro-10-[bis(ethoxy carbonyl)methylene]anthrone, 1,8-dihydroxy-10-[bis(ethoxycar-

bonyl)methylene]anthrone, and 1-cyano-10-[bis(ethoxycarbonyl)methylene]anthrone, 7-nitro-2-aza-9-fluorenylidene-malononitrile, diphenoquinone derivatives, benzoquinone derivatives, naphthoquinone derivatives, quinine derivatives, tetracyanoethylenecyanoethylene, 2,4,8-trinitro thioxantone, dinitrobenzene derivatives, dinitroanthracene derivatives, dinitroacridine derivatives, nitroanthraquinone derivatives, dinitroanthraquinone derivatives, succinic anhydride, maleic anhydride, dibromo maleic anhydride, pyrene derivatives, carbazole derivatives, hydrazone derivatives, N,N-dialkylaniline derivatives, diphenylamine derivatives, triphenylamine derivatives, triphenylmethane derivatives, tetracyano quinodimethane, 2,4,5,7-tetranitro-9-fluorenone, 2,4,7-trinitro-9-dicyanomethylene fluorenone, 2,4,5,7-tetranitroxanthone derivatives, 2,4,8-trinitrothioxanthone derivatives, 1,4,5,8-naphthalene bis-dicarboximide derivatives as described in U.S. Pat. Nos. 5,232,800, 4,468,444, and 4,442,193 and phenylazoquinolide derivatives as described in U.S. Pat. No. 6,472,514. In some embodiments of interest, the electron transport compound comprises an (alkoxycarbonyl-9-fluorenylidene)malononitrile derivative, such as (4-n-butoxycarbonyl-9-fluorenylidene)malononitrile, and 1,4,5,8-naphthalene bis-dicarboximide derivatives.

Although there are many charge transport materials available, there is a need for other charge transport materials to meet the various requirements of particular electrophotography applications.

In electrophotography applications, a charge-generating compound within an organophotoreceptor absorbs light to form electron-hole pairs. These electrons and holes can be transported over an appropriate time frame under a large electric field to discharge locally a surface charge that is generating the field. The discharge of the field at a particular location results in a surface charge pattern that essentially matches the pattern drawn with the light. This charge pattern then can be used to guide toner deposition. The charge transport materials described herein are especially effective at transporting charge, and in particular holes from the electron-hole pairs formed by the charge generating compound. In some embodiments, a specific electron transport compound or charge transport compound can also be used along with the charge transport material of this invention.

The layer or layers of materials containing the charge generating compound and the charge transport materials are within an organophotoreceptor. To print a two dimensional image using the organophotoreceptor, the organophotoreceptor has a two dimensional surface for forming at least a portion of the image. The imaging process then continues by cycling the organophotoreceptor to complete the formation of the entire image and/or for the processing of subsequent images.

The organophotoreceptor may be provided in the form of a plate, a flexible belt, a disk, a rigid drum, a sheet around a rigid or compliant drum, or the like. The charge transport material can be in the same layer as the charge generating compound and/or in a different layer from the charge generating compound. Additional layers can be used also, as described further below.

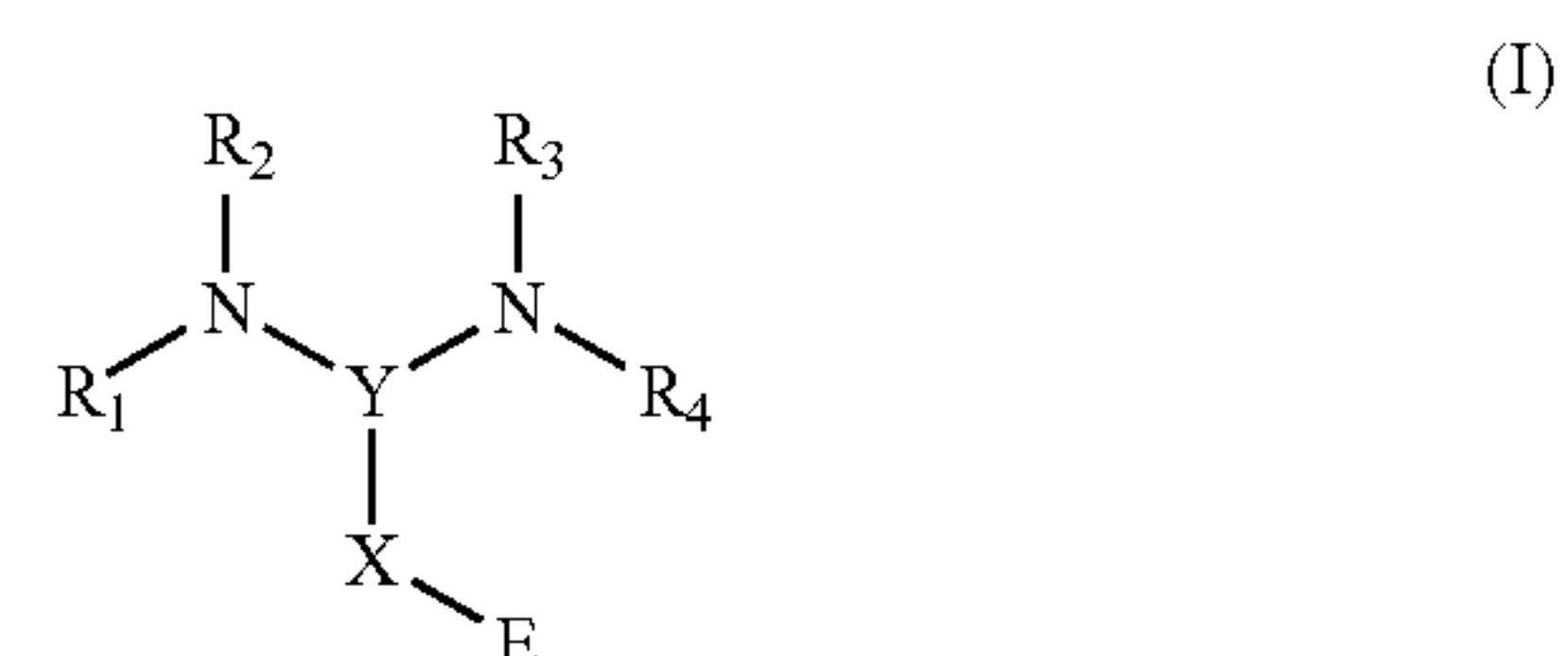
In some embodiments, the organophotoreceptor material comprises, for example: (a) a charge transport layer comprising the charge transport material and a polymeric binder; (b) a charge generating layer comprising the charge generating compound and a polymeric binder; and (c) the electrically conductive substrate. The charge transport layer may be intermediate between the charge generating layer and the electrically conductive substrate. Alternatively, the charge

generating layer may be intermediate between the charge transport layer and the electrically conductive substrate. In further embodiments, the organophotoreceptor material has a single layer with both a charge transport material and a charge generating compound within a polymeric binder.

The organophotoreceptors can be incorporated into an electrophotographic imaging apparatus, such as laser printers. In these devices, an image is formed from physical embodiments and converted to a light image that is scanned onto the organophotoreceptor to form a surface latent image. The surface latent image can be used to attract toner onto the surface of the organophotoreceptor, in which the toner image is the same or the negative of the light image projected onto the organophotoreceptor. The toner can be a liquid toner or a dry toner. The toner is subsequently transferred, from the surface of the organophotoreceptor, to a receiving surface, such as a sheet of paper. After the transfer of the toner, the surface is discharged, and the material is ready to cycle again. The imaging apparatus can further comprise, for example, a plurality of support rollers for transporting a paper receiving medium and/or for movement of the photoreceptor, a light imaging component with suitable optics to form the light image, a light source, such as a laser, a toner source and delivery system and an appropriate control system.

An electrophotographic imaging process generally can comprise (a) applying an electrical charge to a surface of the above-described organophotoreceptor; (b) imagewise exposing the surface of the organophotoreceptor to radiation to dissipate charge in selected areas and thereby form a pattern of charged and uncharged areas on the surface; (c) exposing the surface with a toner, such as a liquid toner that includes a dispersion of colorant particles in an organic liquid to create a toner image, to attract toner to the charged or discharged regions of the organophotoreceptor; and (d) transferring the toner image to a substrate.

As described herein, an organophotoreceptor comprises a charge transport material having the formula:



where Y comprises an aromatic heterocyclic group;

X is a bond or a linking group, such as a $-(\text{CH}_2)_m-$ group, where m is an integer between 1 and 20, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group, a BR_g group, or a $\text{P}(=\text{O})\text{R}_h$ group, where R_a , R_b , R_c , R_d , R_e , R_f , R_g , and R_h are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an acyl group, an alkoxy group, an alkylsulfanyl group, an alkenyl group, such as a vinyl group, an allyl group, and a 2-phenylethenyl group, an alkynyl group, a heterocyclic group, an aromatic group, a part of a ring group, such as cycloalkyl groups, heterocyclic groups, and a benzo group, or an alkyl group where one or more of the hydrogens of the alkyl group is optionally replaced by an aromatic group, a hydroxyl group, a thiol group, a carboxyl group, an amino group, or a halogen;

E comprises a reactive ring group, such as an epoxy group, a thiiranyl group, an aziridinyl group, and an oxetanyl group, a reactive functional group, such as a hydroxyl group, a thiol group, a carboxyl group, and an amino group, or an ethylenically unsaturated group, such as a vinyl ether group, an alkene group, acrylate group, a methacrylate group, an acrylamide group, and a methacrylamide group; and

R_1 , R_2 , R_3 , and R_4 comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group such as cycloalkyl groups, heterocyclic groups, and a benzo group.

A heterocyclic group includes any monocyclic or polycyclic (e.g., bicyclic, tricyclic, etc.) ring compound having at least a heteroatom (e.g., O, S, N, P, B, Si, etc.) in the ring.

An aromatic group can be any conjugated ring system containing $4n+2$ pi-electrons. There are many criteria available for determining aromaticity. A widely employed criterion for the quantitative assessment of aromaticity is the resonance energy. Specifically, an aromatic group has a resonance energy. In some embodiments, the resonance energy of the aromatic group is at least 10 KJ/mol. In further embodiments, the resonance energy of the aromatic group is greater than 0.1 KJ/mol. Aromatic groups may be classified as an aromatic heterocyclic group which contains at least a heteroatom in the $4n+2$ pi-electron ring, or as an aryl group which does not contain a heteroatom in the $4n+2$ pi-electron ring. The aromatic group may comprise a combination of aromatic heterocyclic group and aryl group. Nonetheless, either the aromatic heterocyclic or the aryl group may have at least one heteroatom in a substituent attached to the $4n+2$ pi-electron ring. Furthermore, either the aromatic heterocyclic or the aryl group may comprise a monocyclic or polycyclic (such as bicyclic, tricyclic, etc.) ring.

Non-limiting examples of the aromatic heterocyclic group are furanyl, thiophenyl, pyrrolyl, indolyl, carbazolyl, benzofuranyl, benzothiophenyl, dibenzofuranyl, dibenzothiophenyl, pyridinyl, pyridazinyl, pyrimidinyl, pyrazinyl, triazinyl, tetrazinyl, petazinyl, quinolinyl, isoquinolinyl, cinolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, naphthyridinyl, acridinyl, phenanthridinyl, phenanthrolinyl, anthyridinyl, purinyl, pteridinyl, alloxazinyl, phenazinyl, 5,10-dihydrophenazinyl, phenothiazinyl, phenoxazinyl, phenoxathiinyl, dibenzo(1,4)dioxinyl, thianthrenyl, and a combination thereof. The aromatic heterocyclic group may also include any combination of the above aromatic heterocyclic groups bonded together either by a bond (as in bicarbazolyl) or by a linking group (as in 1,6 di(10H-10-phenothiazinyl)hexane). The linking group may include an aliphatic group, an aromatic group, a heterocyclic group, or a combination thereof. Furthermore, the linking group may comprise at least one heteroatom such as O, S, Si, and N.

Non-limiting examples of the aryl group are phenyl, naphthyl, benzyl, or tolanyl group, sexiphenylene, phenanthrenyl, anthracenyl, coronenyl, and tolanylphenyl. The aryl group may also include any combination of the above aryl groups bonded together either by a bond (as in biphenyl group) or by a linking group (as in stilbenyl, diphenyl sulfone, an arylamino group such as (N,N-disubstituted) arylamino group). The linking group may include an aliphatic group, an aromatic group, a heterocyclic group, or a combination thereof. Furthermore, the linking group may comprise at least one heteroatom such as O, S, Si, and N.

Substitution is liberally allowed on the chemical groups to affect various physical effects on the properties of the compounds, such as mobility, sensitivity, solubility, stability, and the like, as is known generally in the art. In the

description of chemical substituents, there are certain practices common to the art that are reflected in the use of language. The term group indicates that the generically recited chemical entity (e.g., alkyl group, alkenyl group, aryl group, phenyl group, aromatic heterocyclic group, etc.) may have any substituent thereon which is consistent with the bond structure of that group. For example, where the term 'alkyl group' or 'alkenyl group' is used, that term would not only include unsubstituted linear, branched and cyclic alkyl group or alkenyl group, such as methyl, ethyl, ethenyl or vinyl, isopropyl, tert-butyl, cyclohexyl, cyclohexenyl, dodecyl and the like, but also substituents having heteroatom(s), such as 3-ethoxylpropyl, 4-(N,N-diethylamino)butyl, 3-hydroxypentyl, 2-thio]hexyl, 1,2,3-tribromopropyl, and the like, and aromatic group, such as phenyl, naphthyl, carbazolyl, pyrrole, and the like. However, as is consistent with such nomenclature, no substitution would be included within the term that would alter the fundamental bond structure of the underlying group. For example, where a phenyl group is recited, substitution such as 2- or 4-aminophenyl, 2- or 4-(N,N-disubstituted)aminophenyl, 2,4-dihydroxyphenyl, 2,4,6-trithiophenyl, 2,4,6-trimethoxyphenyl and the like would be acceptable within the terminology, while substitution of 1,1,2,2,3,3-hexamethylphenyl would not be acceptable as that substitution would require the ring bond structure of the phenyl group to be altered to a non-aromatic form. Where the term moiety is used, such as alkyl moiety or phenyl moiety, that terminology indicates that the chemical material is not substituted. Where the term alkyl moiety is used, that term represents only an unsubstituted alkyl hydrocarbon group, whether branched, straight chain, or cyclic.

Organophotoreceptors

The organophotoreceptor may be, for example, in the form of a plate, a sheet, a flexible belt, a disk, a rigid drum, or a sheet around a rigid or compliant drum, with flexible belts and rigid drums generally being used in commercial embodiments. The organophotoreceptor may comprise, for example, an electrically conductive substrate and on the electrically conductive substrate a photoconductive element in the form of one or more layers. The photoconductive element can comprise both a charge transport material and a charge generating compound in a polymeric binder, which may or may not be in the same layer, as well as a second charge transport material such as a charge transport compound or an electron transport compound in some embodiments. For example, the charge transport material and the charge generating compound can be in a single layer. In other embodiments, however, the photoconductive element comprises a bilayer construction featuring a charge generating layer and a separate charge transport layer. The charge generating layer may be located intermediate between the electrically conductive substrate and the charge transport layer. Alternatively, the photoconductive element may have a structure in which the charge transport layer is intermediate between the electrically conductive substrate and the charge generating layer.

The electrically conductive substrate may be flexible, for example in the form of a flexible web or a belt, or inflexible, for example in the form of a drum. A drum can have a hollow cylindrical structure that provides for attachment of the drum to a drive that rotates the drum during the imaging process. Typically, a flexible electrically conductive substrate comprises an electrically insulating substrate and a thin layer of electrically conductive material onto which the photoconductive material is applied.

The electrically insulating substrate may be paper or a film forming polymer such as polyester (e.g., polyethylene terephthalate or polyethylene naphthalate), polyimide, polysulfone, polypropylene, nylon, polyester, polycarbonate, polyvinyl resin, polyvinyl fluoride, polystyrene and the like. Specific examples of polymers for supporting substrates included, for example, polyethersulfone (STABAR™ S-100, available from ICI), polyvinyl fluoride (Tedlar®, available from E.I. DuPont de Nemours & Company), polybisphenol-A polycarbonate (MAKROFOL™, available from Mobay Chemical Company) and amorphous polyethylene terephthalate (MELINAR™, available from ICI Americas, Inc.). The electrically conductive materials may be graphite, dispersed carbon black, iodine, conductive polymers such as polypyrroles and Calgon® conductive polymer 261 (commercially available from Calgon Corporation, Inc., Pittsburgh, Pa.), metals such as aluminum, titanium, chromium, brass, gold, copper, palladium, nickel, or stainless steel, or metal oxide such as tin oxide or indium oxide. In embodiments of particular interest, the electrically conductive material is aluminum. Generally, the photoconductor substrate has a thickness adequate to provide the required mechanical stability. For example, flexible web substrates generally have a thickness from about 0.01 to about 1 mm, while drum substrates generally have a thickness from about 0.5 mm to about 2 mm.

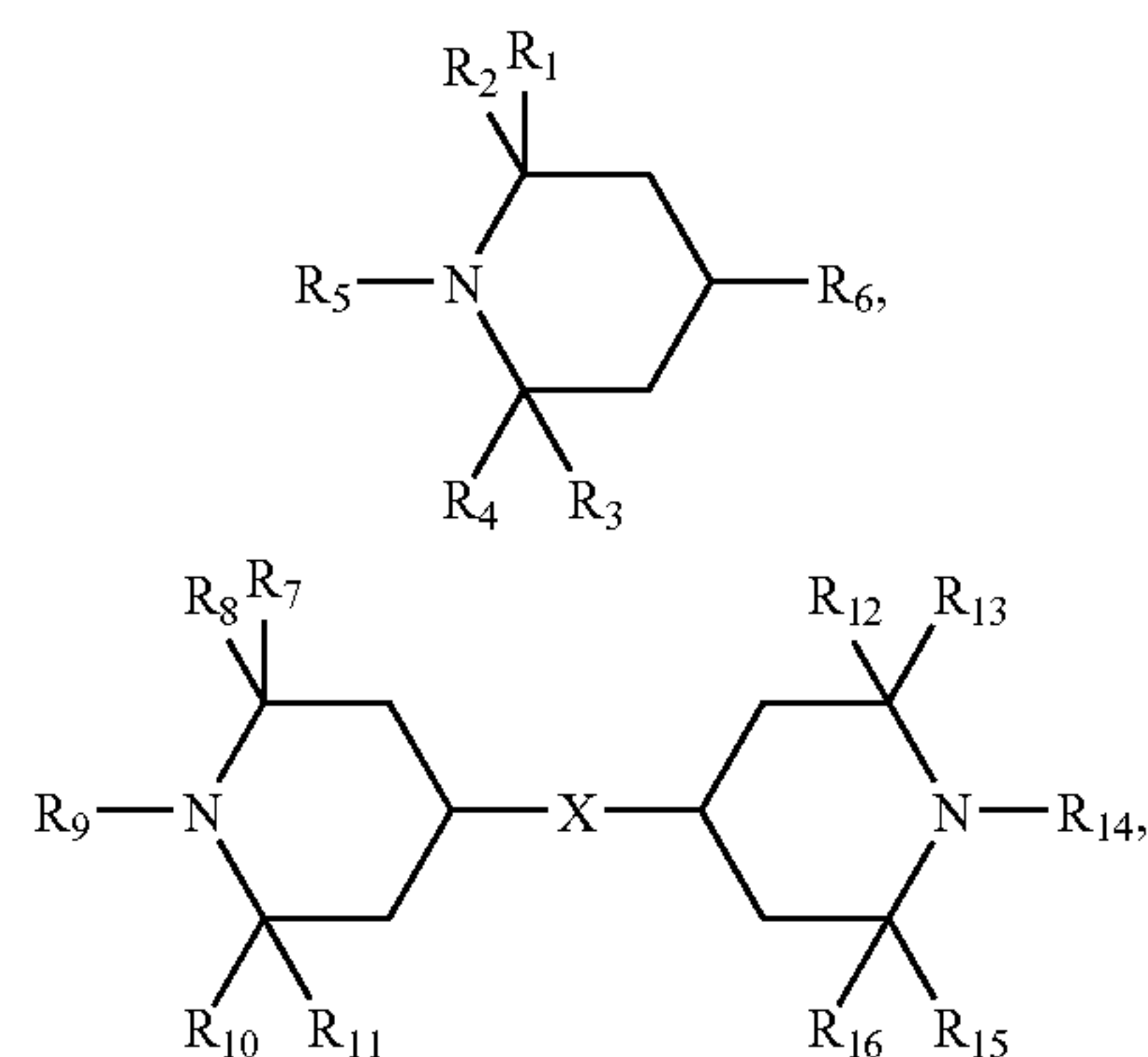
The charge generating compound is a material that is capable of absorbing light to generate charge carriers (such as a dye or pigment). Non-limiting examples of suitable charge generating compounds include, for example, metal-free phthalocyanines (e.g., ELA 8034 metal-free phthalocyanine available from H.W. Sands, Inc. or Sanyo Color Works, Ltd., CGM-X01), metal phthalocyanines such as titanium phthalocyanine, copper phthalocyanine, oxytitanium phthalocyanine (also referred to as titanyl oxyphthalocyanine, and including any crystalline phase or mixtures of crystalline phases that can act as a charge generating compound), hydroxygallium phthalocyanine, squarylium dyes and pigments, hydroxy-substituted squarylium pigments, perylimides, polynuclear quinones available from Allied Chemical Corporation under the trade name INDOFAST™ Double Scarlet, INDOFAST™ Violet Lake B, INDOFAST™ Brilliant Scarlet and INDOFAST™ Orange, quinacridones available from DuPont under the trade name MONASTRAL™ Red, MONASTRAL™ Violet and MONASTRAL™ Red Y, naphthalene 1,4,5,8-tetracarboxylic acid derived pigments including the perinones, tetrabenzoporphyrins and tetranaphthaloporphyrins, indigo- and thioindigo dyes, benzothioxanthene-derivatives, perylene 3,4,9,10-tetracarboxylic acid derived pigments, polyazo-pigments including bisazo-, trisazo- and tetrakisazo-pigments, polymethine dyes, dyes containing quinazoline groups, tertiary amines, amorphous selenium, selenium alloys such as selenium-tellurium, selenium-tellurium-arsenic and selenium-arsenic, cadmium sulphoselenide, cadmium selenide, cadmium sulphide, and mixtures thereof. For some embodiments, the charge generating compound comprises oxytitanium phthalocyanine (e.g., any phase thereof), hydroxygallium phthalocyanine or a combination thereof.

The photoconductive layer of this invention may optionally contain a second charge transport material which may be a charge transport compound, an electron transport compound, or a combination of both. Generally, any charge transport compound or electron transport compound known in the art can be used as the second charge transport material.

An electron transport compound and a UV light stabilizer can have a synergistic relationship for providing desired electron flow within the photoconductor. The presence of the UV light stabilizers alters the electron transport properties of the electron transport compounds to improve the electron transporting properties of the composite. UV light stabilizers can be ultraviolet light absorbers or ultraviolet light inhibitors that trap free radicals.

UV light absorbers can absorb ultraviolet radiation and dissipate it as heat. UV light inhibitors are thought to trap free radicals generated by the ultraviolet light and after trapping of the free radicals, subsequently to regenerate active stabilizer moieties with energy dissipation. In view of the synergistic relationship of the UV stabilizers with electron transport compounds, the particular advantages of the UV stabilizers may not be their UV stabilizing abilities, although the UV stabilizing ability may be further advantageous in reducing degradation of the organophotoreceptor over time. The improved synergistic performance of organophotoreceptors with layers comprising both an electron transport compound and a UV stabilizer are described further in copending U.S. patent application Ser. No. 10/425,333 filed on Apr. 28, 2003 to Zhu, entitled "Organophotoreceptor With A Light Stabilizer," incorporated herein by reference.

Non-limiting examples of suitable light stabilizer include, for example, hindered trialkylamines such as Tinuvin 144 and Tinuvin 292 (from Ciba Specialty Chemicals, Terrytown, N.Y.), hindered alkoxydialkylamines such as Tinuvin 123 (from Ciba Specialty Chemicals), benzotriazoles such as Tinuvin 328, Tinuvin 900 and Tinuvin 928 (from Ciba Specialty Chemicals), benzophenones such as Sanduvor 3041 (from Clariant Corp., Charlotte, N.C.), nickel compounds such as Arbestab (from Robinson Brothers Ltd, West Midlands, Great Britain), salicylates, cyanocinnamates, benzylidene malonates, benzoates, oxanilides such as Sanduvor VSU (from Clariant Corp., Charlotte, N.C.), triazines such as Cyagard UV-1164 (from Cytec Industries Inc., N.J.), polymeric sterically hindered amines such as Luchem (from Atochem North America, Buffalo, N.Y.). In some embodiments, the light stabilizer is selected from the group consisting of hindered trialkylamines having the following formula:



where R₁, R₂, R₃, R₄, R₆, R₇, R₈, R₁₀, R₁₁, R₁₂, R₁₃, R₁₄, R₁₅ are, each independently, hydrogen, alkyl group, or ester, or ether group; and R₅, R₉, and R₁₄ are, each independently, alkyl group; and X is a linking group selected from the group consisting of —O—CO—(CH₂)_m—CO—O— where m is between 2 to 20.

The binder generally is capable of dispersing or dissolving the charge transport material (in the case of the charge transport layer or a single layer construction), the charge generating compound (in the case of the charge generating layer or a single layer construction) and/or an electron transport compound for appropriate embodiments. Examples of suitable binders for both the charge generating layer and charge transport layer generally include, for example, poly(styrene-co-butadiene), poly(styrene-co-acrylonitrile), modified acrylic polymers, poly(vinyl acetate), styrene-alkyd resins, soya-alkyl resins, poly(vinyl chloride), poly(vinylidene chloride), polyacrylonitrile, polycarbonates, poly(acrylic acid), polyacrylates, polymethacrylates, styrene polymers, poly(vinyl butyral), alkyd resins, polyamides, polyurethanes, polyesters, polysulfones, polyethers, polyketones, phenoxy resins, epoxy resins, silicone resins, polysiloxanes, poly(hydroxyether) resins, poly(hydroxystyrene) resins, novolak, poly(phenylglycidyl ether-co-dicyclopentadiene), copolymers of monomers used in the above-mentioned polymers, and combinations thereof. Specific suitable binders include, for example, poly(vinyl butyral), polycarbonate, and polyester. Non-limiting examples of poly(vinyl butyral) include BX-1 and BX-5 from Sekisui Chemical Co. Ltd., Japan. Non-limiting examples of suitable polycarbonate include polycarbonate A which is derived from bisphenol-A (e.g. Iupilon-A from Mitsubishi Engineering Plastics, or Lexan 145 from General Electric); polycarbonate Z which is derived from cyclohexylidene bisphenol (e.g. Iupilon-Z from Mitsubishi Engineering Plastics Corp, White Plain, N.Y.); and polycarbonate C which is derived from methylbisphenol A (from Mitsubishi Chemical Corporation). Non-limiting examples of suitable polyester binders include ortho-poly(ethylene terephthalate) (e.g. OPET TR-4 from Kanebo Ltd., Yamaguchi, Japan).

Suitable optional additives for any one or more of the layers include, for example, antioxidants, coupling agents, dispersing agents, curing agents, surfactants, and combinations thereof.

The photoconductive element overall typically has a thickness from about 10 microns to about 45 microns. In the dual layer embodiments having a separate charge generating layer and a separate charge transport layer, charge generation layer generally has a thickness from about 0.5 microns to about 2 microns, and the charge transport layer has a thickness from about 5 microns to about 35 microns. In embodiments in which the charge transport material and the charge generating compound are in the same layer, the layer with the charge generating compound and the charge transport composition generally has a thickness from about 7 microns to about 30 microns. In embodiments with a distinct electron transport layer, the electron transport layer has an average thickness from about 0.5 microns to about 10 microns and in further embodiments from about 1 micron to about 3 microns. In general, an electron transport overcoat layer can increase mechanical abrasion resistance, increases resistance to carrier liquid and atmospheric moisture, and decreases degradation of the photoreceptor by corona gases. A person of ordinary skill in the art will recognize that additional ranges of thickness within the explicit ranges above are contemplated and are within the present disclosure.

Generally, for the organophotoreceptors described herein, the charge generation compound is in an amount from about 0.5 to about 25 weight percent, in further embodiments in an amount from about 1 to about 15 weight percent, and in other embodiments in an amount from about 2 to about 10 weight percent, based on the weight of the photoconductive

layer. The charge transport material is in an amount from about 10 to about 80 weight percent, based on the weight of the photoconductive layer, in further embodiments in an amount from about 35 to about 60 weight percent, and in other embodiments from about 45 to about 55 weight percent, based on the weight of the photoconductive layer. The optional second charge transport material, when present, can be in an amount of at least about 2 weight percent, in other embodiments from about 2.5 to about 25 weight percent, based on the weight of the photoconductive layer, and in further embodiments in an amount from about 4 to about 20 weight percent, based on the weight of the photoconductive layer. The binder is in an amount from about 15 to about 80 weight percent, based on the weight of the photoconductive layer, and in further embodiments in an amount from about 20 to about 75 weight percent, based on the weight of the photoconductive layer. A person of ordinary skill in the art will recognize that additional ranges within the explicit ranges of compositions are contemplated and are within the present disclosure.

For the dual layer embodiments with a separate charge generating layer and a charge transport layer, the charge generation layer generally comprises a binder in an amount from about 10 to about 90 weight percent, in further embodiments from about 15 to about 80 weight percent and in some embodiments in an amount from about 20 to about 75 weight percent, based on the weight of the charge generation layer. The optional charge transport material in the charge generating layer, if present, generally can be in an amount of at least about 2.5 weight percent, in further embodiments from about 4 to about 30 weight percent and in other embodiments in an amount from about 10 to about 25 weight percent, based on the weight of the charge generating layer. The charge transport layer generally comprises a binder in an amount from about 20 weight percent to about 70 weight percent and in further embodiments in an amount from about 30 weight percent to about 50 weight percent. A person of ordinary skill in the art will recognize that additional ranges of binder concentrations for the dual layer embodiments within the explicit ranges above are contemplated and are within the present disclosure.

For the embodiments with a single layer having a charge generating compound and a charge transport material, the photoconductive layer generally comprises a binder, a charge transport material, and a charge generation compound. The charge generation compound can be in an amount from about 0.05 to about 25 weight percent and in further embodiment in an amount from about 2 to about 15 weight percent, based on the weight of the photoconductive layer. The charge transport material can be in an amount from about 10 to about 80 weight percent, in other embodiments from about 25 to about 65 weight percent, in additional embodiments from about 30 to about 60 weight percent and in further embodiments in an amount from about 35 to about 55 weight percent, based on the weight of the photoconductive layer, with the remainder of the photoconductive layer comprising the binder, and optionally additives, such as any conventional additives. A single layer with a charge transport composition and a charge generating compound generally comprises a binder in an amount from about 10 weight percent to about 75 weight percent, in other embodiments from about 20 weight percent to about 60 weight percent, and in further embodiments from about 25 weight percent to about 50 weight percent. Optionally, the layer with the charge generating compound and the charge transport material may comprise a second charge transport material. The optional second charge transport material, if

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present, generally can be in an amount of at least about 2.5 weight percent, in further embodiments from about 4 to about 30 weight percent and in other embodiments in an amount from about 10 to about 25 weight percent, based on the weight of the photoconductive layer. A person of ordinary skill in the art will recognize that additional composition ranges within the explicit composition ranges for the layers above are contemplated and are within the present disclosure.

In general, any layer with an electron transport layer can advantageously further include a UV light stabilizer. In particular, the electron transport layer generally can comprise an electron transport compound, a binder, and an optional UV light stabilizer. An overcoat layer comprising an electron transport compound is described further in copending U.S. patent application Ser. No. 10/396,536 to Zhu et al. entitled, "Organophotoreceptor With An Electron Transport Layer," incorporated herein by reference. For example, an electron transport compound as described above may be used in the release layer of the photoconductors described herein. The electron transport compound in an electron transport layer can be in an amount from about 10 to about 50 weight percent, and in other embodiments in an amount from about 20 to about 40 weight percent, based on the weight of the electron transport layer. A person of ordinary skill in the art will recognize that additional ranges of compositions within the explicit ranges are contemplated and are within the present disclosure.

The UV light stabilizer, if present, in any one or more appropriate layers of the photoconductor generally is in an amount from about 0.5 to about 25 weight percent and in some embodiments in an amount from about 1 to about 10 weight percent, based on the weight of the particular layer. A person of ordinary skill in the art will recognize that additional ranges of compositions within the explicit ranges are contemplated and are within the present disclosure.

For example, the photoconductive layer may be formed by dispersing or dissolving the components, such as one or more of a charge generating compound, the charge transport material of this invention, a second charge transport material such as a charge transport compound or an electron transport compound, a UV light stabilizer, and a polymeric binder in organic solvent, coating the dispersion and/or solution on the respective underlying layer and drying the coating. In particular, the components can be dispersed by high shear homogenization, ball-milling, attritor milling, high energy bead (sand) milling or other size reduction processes or mixing means known in the art for effecting particle size reduction in forming a dispersion.

The photoreceptor may optionally have one or more additional layers as well. An additional layer can be, for example, a sub-layer or an overcoat layer, such as a barrier layer, a release layer, a protective layer, or an adhesive layer. A release layer or a protective layer may form the uppermost layer of the photoconductor element. A barrier layer may be sandwiched between the release layer and the photoconductive element or used to overcoat the photoconductive element. The barrier layer provides protection from abrasion to the underlayers. An adhesive layer locates and improves the adhesion between a photoconductive element, a barrier layer and a release layer, or any combination thereof. A sub-layer is a charge blocking layer and locates between the electrically conductive substrate and the photoconductive element. The sub-layer may also improve the adhesion between the electrically conductive substrate and the photoconductive element.

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Suitable barrier layers include, for example, coatings such as crosslinkable siloxanol-colloidal silica coating and hydroxylated silsesquioxane-colloidal silica coating, and organic binders such as poly(vinyl alcohol), methyl vinyl ether/maleic anhydride copolymer, casein, poly(vinyl pyrrolidone), poly(acrylic acid), gelatin, starch, polyurethanes, polyimides, polyesters, polyamides, poly(vinyl acetate), poly(vinyl chloride), poly(vinylidene chloride), polycarbonates, poly(vinyl butyral), poly(vinyl acetoacetal), poly(vinyl formal), polyacrylonitrile, poly(methyl methacrylate), polyacrylates, poly(vinyl carbazoles), copolymers of monomers used in the above-mentioned polymers, vinyl chloride/vinyl acetate/vinyl alcohol terpolymers, vinyl chloride/vinyl acetate/maleic acid terpolymers, ethylene/vinyl acetate copolymers, vinyl chloride/vinylidene chloride copolymers, cellulose polymers, and mixtures thereof. The above barrier layer polymers optionally may contain small inorganic particles such as fumed silica, silica, titania, alumina, zirconia, or a combination thereof. Barrier layers are described further in U.S. Pat. No. 6,001,522 to Woo et al., entitled "Barrier Layer For Photoconductor Elements Comprising An Organic Polymer And Silica," incorporated herein by reference. The release layer topcoat may comprise any release layer composition known in the art. In some embodiments, the release layer is a fluorinated polymer, siloxane polymer, fluorosilicone polymer, silane, polyethylene, polypropylene, polyacrylate, or a combination thereof. The release layers can comprise crosslinked polymers.

The release layer may comprise, for example, any release layer composition known in the art. In some embodiments, the release layer comprises a fluorinated polymer, siloxane polymer, fluorosilicone polymer, polysilane, polyethylene, polypropylene, polyacrylate, poly(methyl methacrylate-co-methacrylic acid), urethane resins, urethane-epoxy resins, acrylated-urethane resins, urethane-acrylic resins, or a combination thereof. In further embodiments, the release layers comprise crosslinked polymers.

The protective layer can protect the organophotoreceptor from chemical and mechanical degradation. The protective layer may comprise any protective layer composition known in the art. In some embodiments, the protective layer is a fluorinated polymer, siloxane polymer, fluorosilicone polymer, polysilane, polyethylene, polypropylene, polyacrylate, poly(methyl methacrylate-co-methacrylic acid), urethane resins, urethane-epoxy resins, acrylated-urethane resins, urethane-acrylic resins, or a combination thereof. In some embodiments of particular interest, the protective layers are crosslinked polymers.

An overcoat layer may comprise an electron transport compound as described further in copending U.S. patent application Ser. No. 10/396,536, filed on Mar. 25, 2003 to Zhu et al. entitled, "Organoreceptor With An Electron Transport Layer," incorporated herein by reference. For example, an electron transport compound, as described above, may be used in the release layer of this invention. The electron transport compound in the overcoat layer can be in an amount from about 2 to about 50 weight percent, and in other embodiments in an amount from about 10 to about 40 weight percent, based on the weight of the release layer. A person of ordinary skill in the art will recognize that additional ranges of composition within the explicit ranges are contemplated and are within the present disclosure.

Generally, adhesive layers comprise a film forming polymer, such as polyester, poly(vinyl butyral), poly(vinyl pyrrolidone), polyurethane, poly(methyl methacrylate), poly(hydroxy amino ether) and the like. Barrier and adhesive layers are described further in U.S. Pat. No. 6,180,305 to

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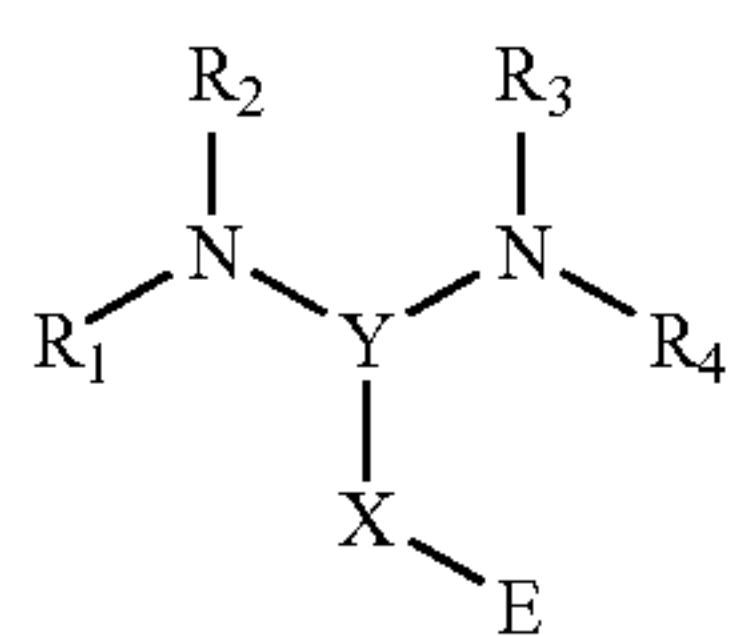
Ackley et al., entitled "Organic Photoreceptors for Liquid Electrophotography," incorporated herein by reference.

Sub-layers can comprise, for example, poly(vinyl butyral), organosilanes, hydrolyzable silanes, epoxy resins, polyesters, polyamides, polyurethanes, cellulose, and the like. In some embodiments, the sub-layer has a dry thickness between about 20 Angstroms and about 20,000 Angstroms. Sublayers containing metal oxide conductive particles can be between about 1 and about 25 microns thick. A person of ordinary skill in the art will recognize that additional ranges of compositions and thickness within the explicit ranges are contemplated and are within the present disclosure.

The charge transport materials as described herein, and photoreceptors including these compounds, are suitable for use in an imaging process with either dry or liquid toner development. For example, any dry toners and liquid toners known in the art may be used in the process and the apparatus of this invention. Liquid toner development can be desirable because it offers the advantages of providing higher resolution images and requiring lower energy for image fixing compared to dry toners. Examples of suitable liquid toners are known in the art. Liquid toners generally comprise toner particles dispersed in a carrier liquid. The toner particles can comprise a colorant/pigment, a resin binder, and/or a charge director. In some embodiments of liquid toner, a resin to pigment ratio can be from 1:1 to 10:1, and in other embodiments, from 4:1 to 8:1. Liquid toners are described further in Published U.S. Patent Applications 2002/0128349, entitled "Liquid Inks Comprising A Stable Organosol," and 2002/0086916, entitled "Liquid Inks Comprising Treated Colorant Particles," and U.S. Pat. No. 6,649, 316, entitled "Phase Change Developer For Liquid Electrophotography," all three of which are incorporated herein by reference.

Charge Transport Material

As described herein, an organophotoreceptor comprises a charge transport material having the formula



where Y comprises an aromatic heterocyclic group;

X is a bond or a linking group, such as a $-(CH_2)_m-$ group, where m is an integer between 1 and 20, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group, a BR_g group, or a $P(=O)R_h$ group, where $R_a, R_b, R_c, R_d, R_e, R_f, R_g,$ and R_h are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an acyl group, an alkoxy group, an alkylsulfanyl group, an alkenyl group, such as a vinyl group, an allyl group, and a 2-phenylethenyl group, an alkynyl group, a heterocyclic group, an aromatic group, a part of a ring group, such as cycloalkyl groups, heterocyclic groups, and a benzo group, or an alkyl group where one or more of the hydrogens of the alkyl group is optionally replaced by an aromatic group, a hydroxyl group, a thiol group, a carboxyl group, an amino group, or a halogen;

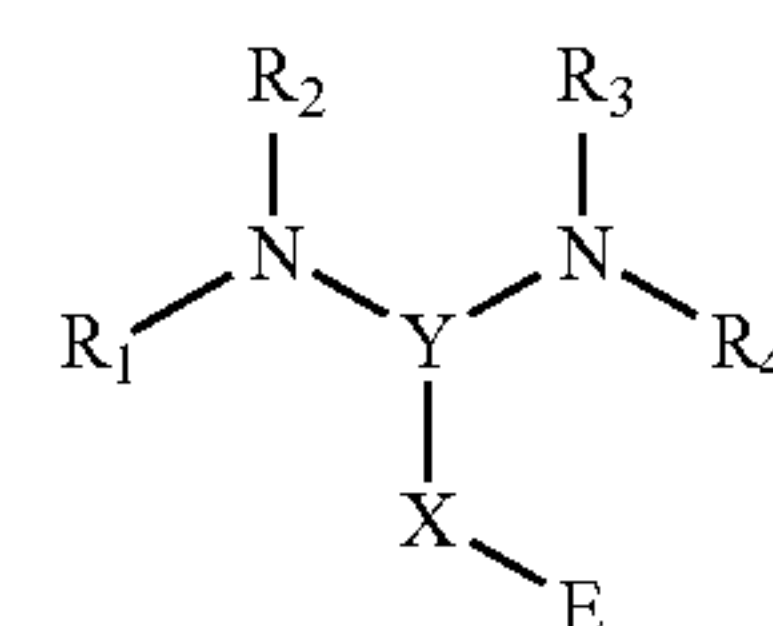
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E comprises a reactive ring group, such as an epoxy group, a thiiranyl group, an aziridinyl group, and an oxetanyl group, a reactive functional group, such as a hydroxyl group, a thiol group, a carboxyl group, and an amino group, or an ethylenically unsaturated group, such as a vinyl ether group, an alkene group, acrylate group, a methacrylate group, an acrylamide group, and a methacrylamide group; and

$R_1, R_2, R_3,$ and R_4 comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group such as cycloalkyl groups, heterocyclic groups, and a benzo group.

In some embodiments, the Y group of the charge transport material of Formula (I) comprises a carbazolyl group, a phenothiazinyl group, a 5,10-dihydrophenazinyl group, a phenoxazinyl group, an indolyl group, or a pyrrolyl group. In other embodiments, the X group of the charge transport material of Formula (I) is a methylene group. In further embodiments, the E group of the charge transport material of Formula (I) comprises an epoxy group, a thiiranyl group, an aziridinyl group, or an oxetanyl group. In additional embodiments, $R_1, R_2, R_3,$ and R_4 of the charge transport material of Formula (I) and $R_1', R_2', R_3',$ and R_4' of Formula (II) comprise, each independently, an alkyl group or an aryl group.

In some embodiments, a bridged charge transport material may be prepared by reacting a bridging compound having a formula HQ_1-Z-Q_2H with at least a compound having a reactive ring group comprising the following formula:



(I)

where Y comprises an aromatic heterocyclic group;

X and Z are, each independently, a bond or a linking group, such as a $-(CH_2)_m-$ group, where m is an integer between 1 and 20, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group, a BR_g group, or a $P(=O)R_h$ group, where $R_a, R_b, R_c, R_d, R_e, R_f, R_g,$ and R_h are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, an acyl group, an alkoxy group, an alkylsulfanyl group, an alkenyl group, such as a vinyl group, an allyl group, and a 2-phenylethenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as cycloalkyl groups, heterocyclic groups, and a benzo group;

E comprises a reactive ring group, such as an epoxy group, a thiiranyl group, an aziridinyl group, and an oxetanyl group, a reactive functional group, such as a hydroxyl group, a thiol group, a carboxyl group, and an amino group, or an ethylenically unsaturated group, such as a vinyl ether group, an alkene group, acrylate group, a methacrylate group, an acrylamide group, and a methacrylamide group;

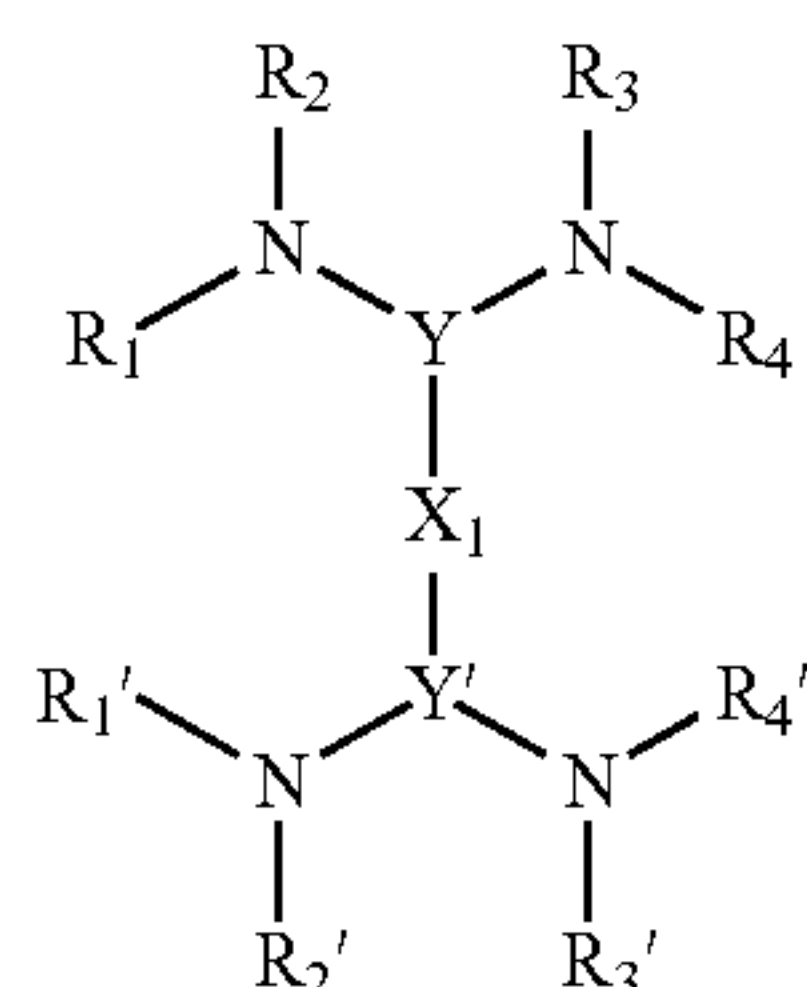
Q_1 and Q_2 are each independently, O, S, and NR; and

$R, R_1, R_2, R_3,$ and R_4 comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group,

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or a part of a ring group such as cycloalkyl groups, heterocyclic groups, and a benzo group.

In other embodiments, the bridged charge transport material prepared by the method above has the following formula:

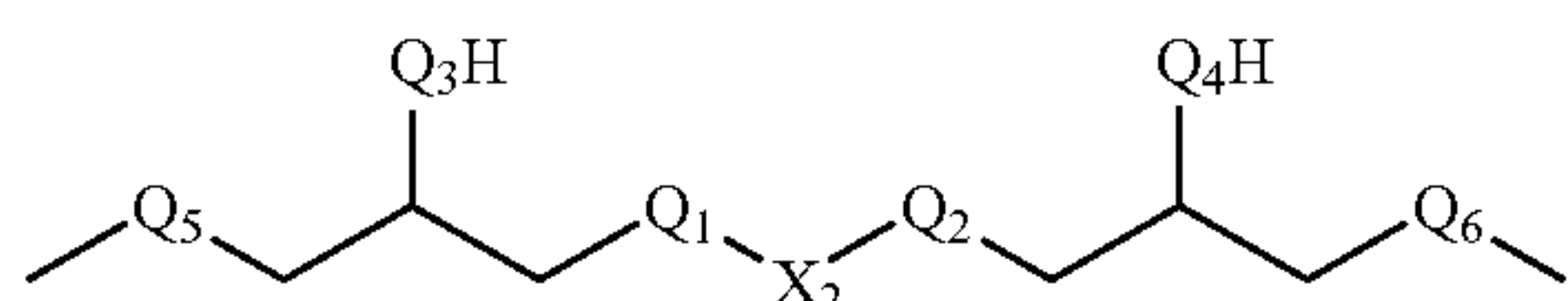


where Y and Y', each independently, comprise an aromatic heterocyclic group;

X₁ is a first linking group, such as a $-(CH_2)_m-$ group, where m is an integer between 1 and 66, inclusive, and one of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group, a BR_g group, or a P(=O)R_h group, where R_a, R_b, R_c, R_d, R_e, R_f, R_g, and R_h are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, an acyl group, an alkoxy group, an alkylsulfanyl group, an alkenyl group, such as a vinyl group, an allyl group, and a 2-phenylethenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as cycloalkyl groups, heterocyclic groups, and a benzo group; and

R₁, R₂, R₃, R₄, R₁', R₂', R₃', and R₄' comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group such as cycloalkyl groups, heterocyclic groups, and a benzo group.

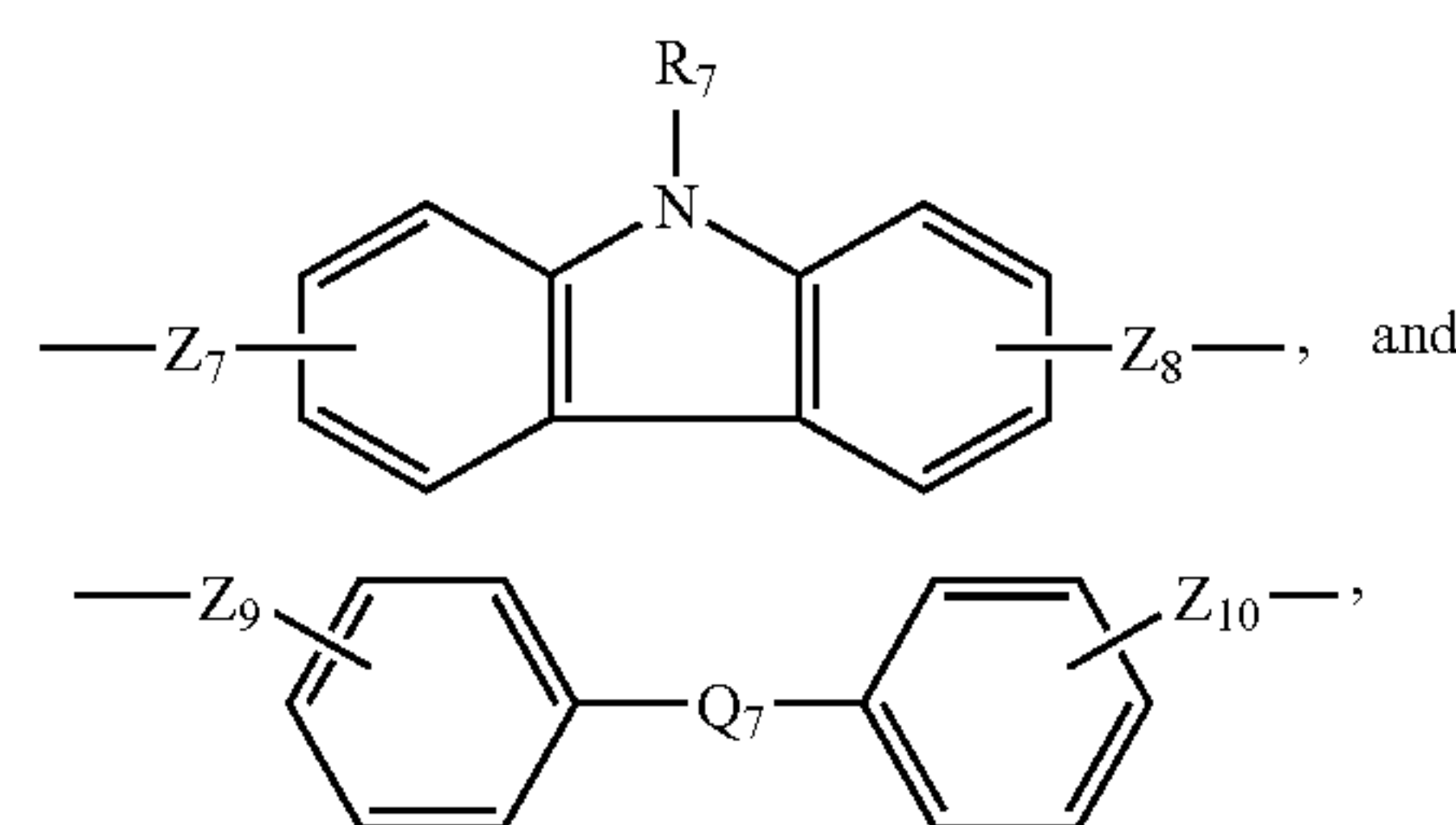
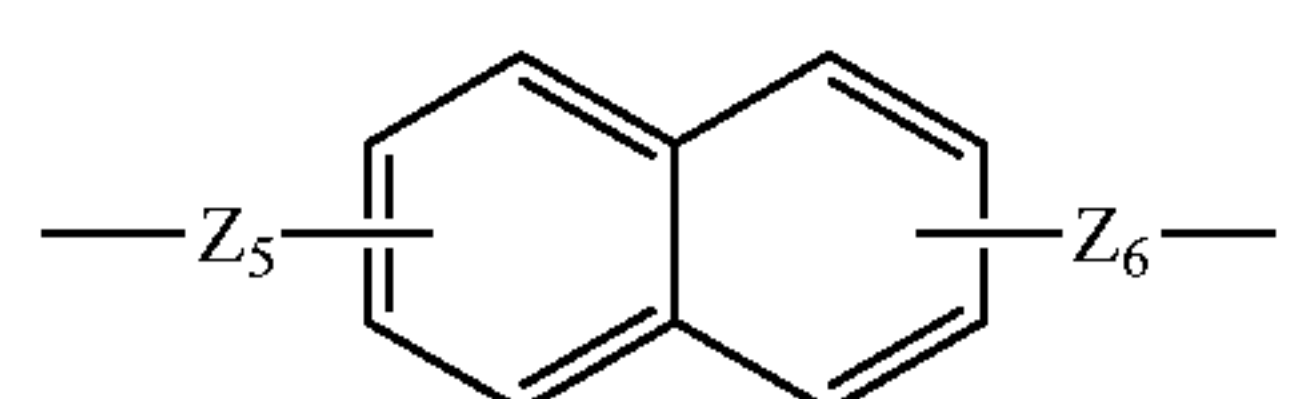
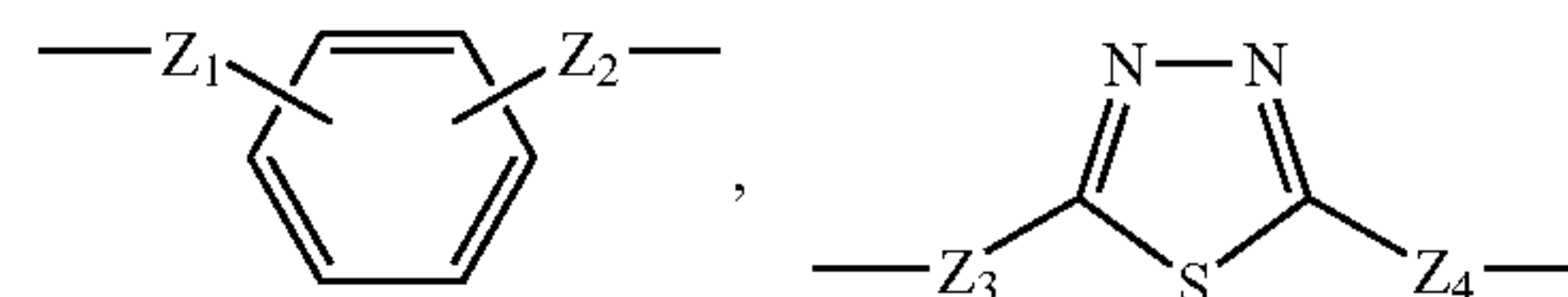
In some embodiments, the Y group and the Y' group of Formula (II), each independently, comprise a carbazolyl group, a phenothiazinyl group, 5,10-dihydrophenazinyl, phenoxazinyl, an indolyl group, or a pyrrolyl group. In other embodiments, R₁, R₂, R₃, R₄, R₁', R₂', R₃', and R₄' of Formula (II) comprise, each independently, an alkyl group or an aryl group. In further embodiments, the X₁ group of Formula (II) has the following formula:



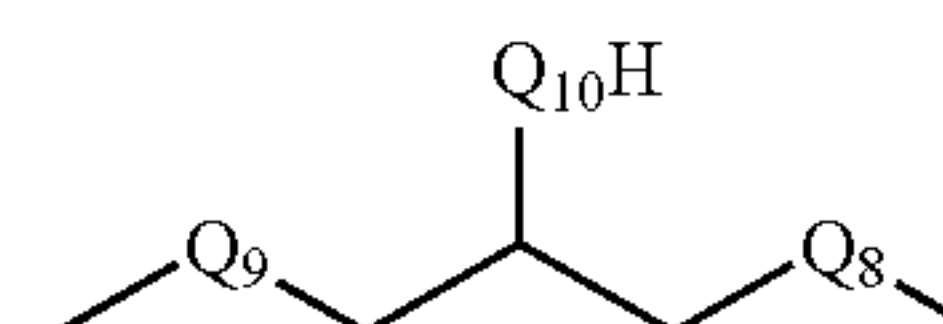
where X₂ comprises a bond or a second linking group; Q₁, Q₂, Q₃, and Q₄ comprise, each independently, O, S, and NR₅; Q₅ and Q₆ comprise, each independently, a bond, O, S, and NR₆; and R₅ and R₆ comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, or an aromatic group. In further embodiments, the X₂ group of Formula (III) comprises a $-(CH_2)_m-$ group, where m is an integer between 1 and 20, inclusive, and at least one of the methylene groups is replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group, a BR_g

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group, or a P(=O)R_h group, where R_a, R_b, R_c, R_d, R_e, R_f, R_g, and R_h are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, an acyl group, an alkoxy group, an alkylsulfanyl group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group. In further embodiments, the X₂ group of Formula (III) is selected from the group consisting of the following formulae:



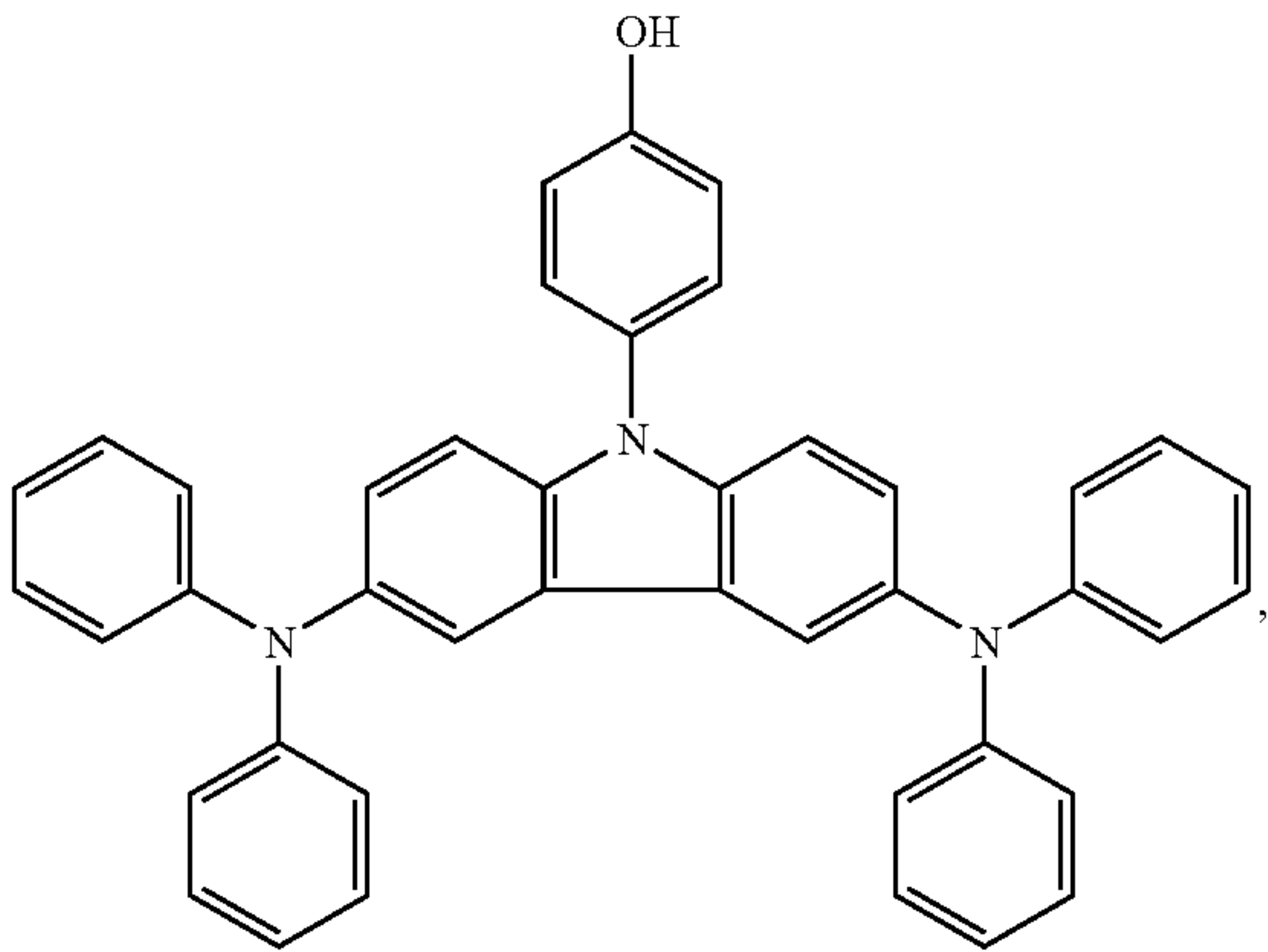
where Q₇ is a bond, O, S, C=O, SO₂, C(=O)O, an NR₈ group, or a CR₉R₁₀ group; R₇, R₈, R₉, and R₁₀ are, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group; and Z₁, Z₂, Z₃, Z₄, Z₅, Z₆, Z₇, Z₈, Z₉, and Z₁₀ are, each independently, a bond or a bridging group, such as a $-(CH_2)_p-$ group, where p is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_i group, a CR_j group, a CR_kR_l group, a SiR_mR_n group, a BR_o group, or a P(=O)R_p group, where R_i, R_j, R_k, R_l, R_m, R_n, R_o, and R_p are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, an acyl group, an alkoxy group, an alkylsulfanyl group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group. In additional embodiments, the X₁ group of Formula (II) has the following formula:



where Q₈, Q₉, and Q₁₀ comprise, each independently, O, S, and NR₇; and R₇ comprises H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, or an aromatic group.

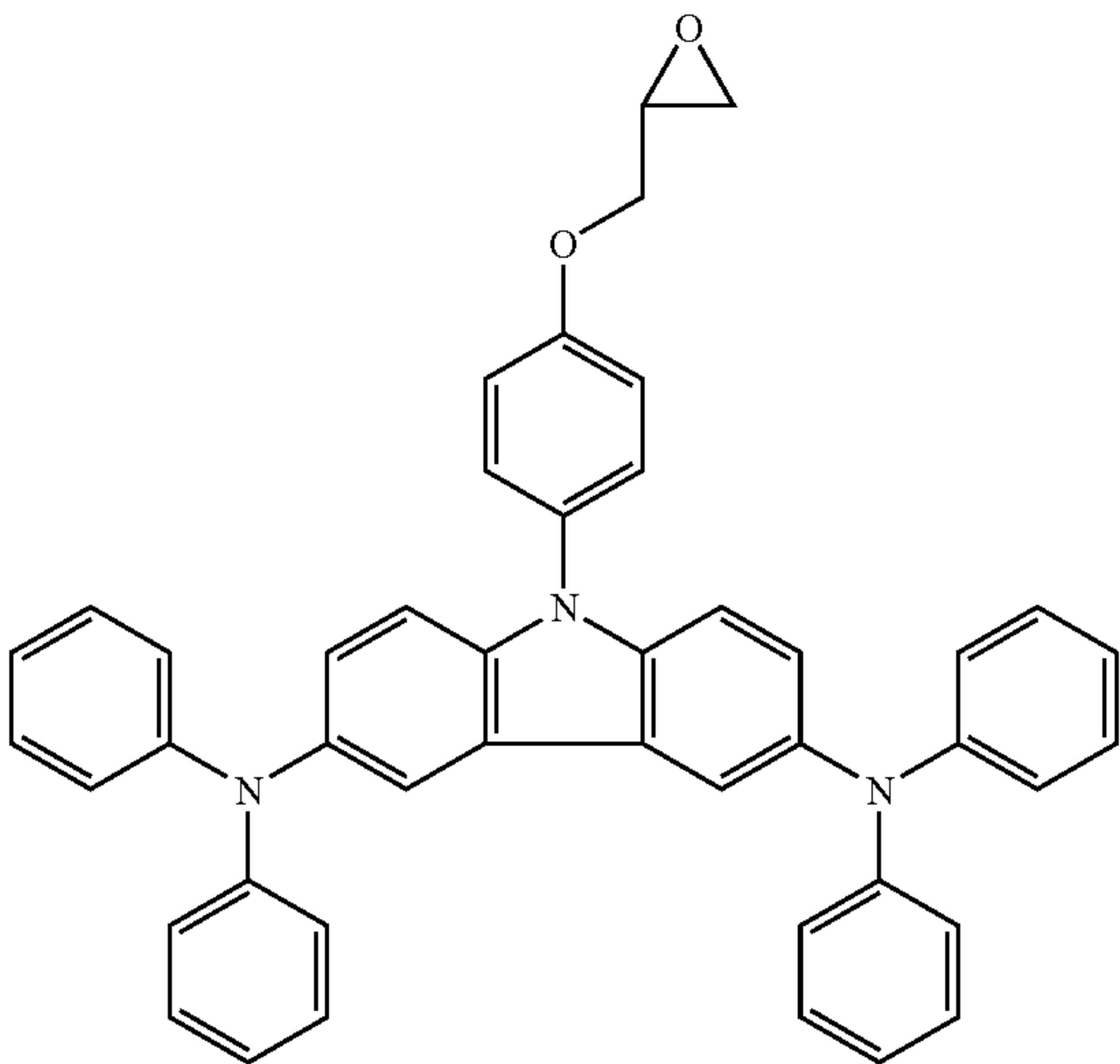
Specific, non-limiting examples of suitable charge transport materials within Formula (I) of the present invention have the following structures:

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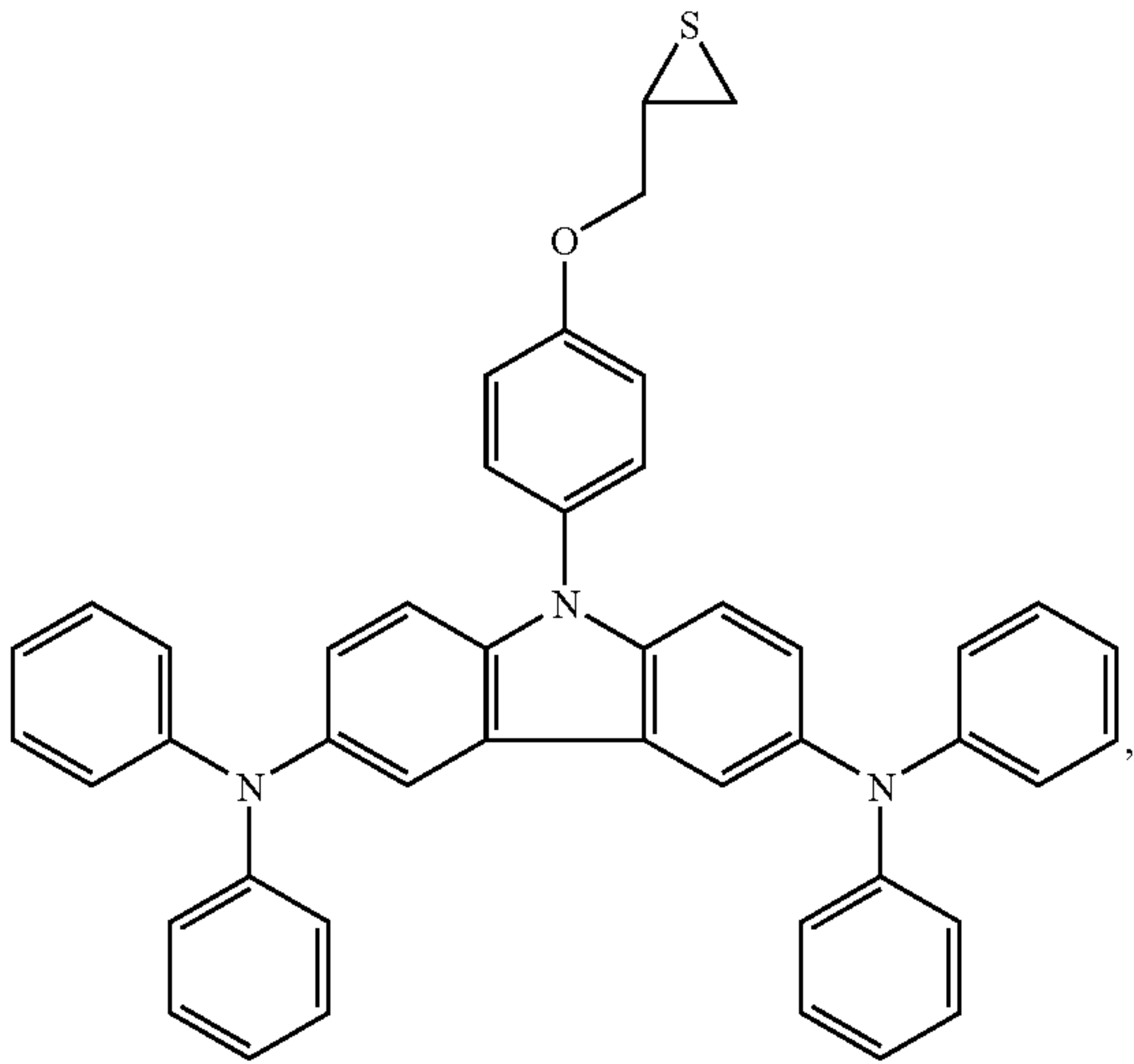
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(1)

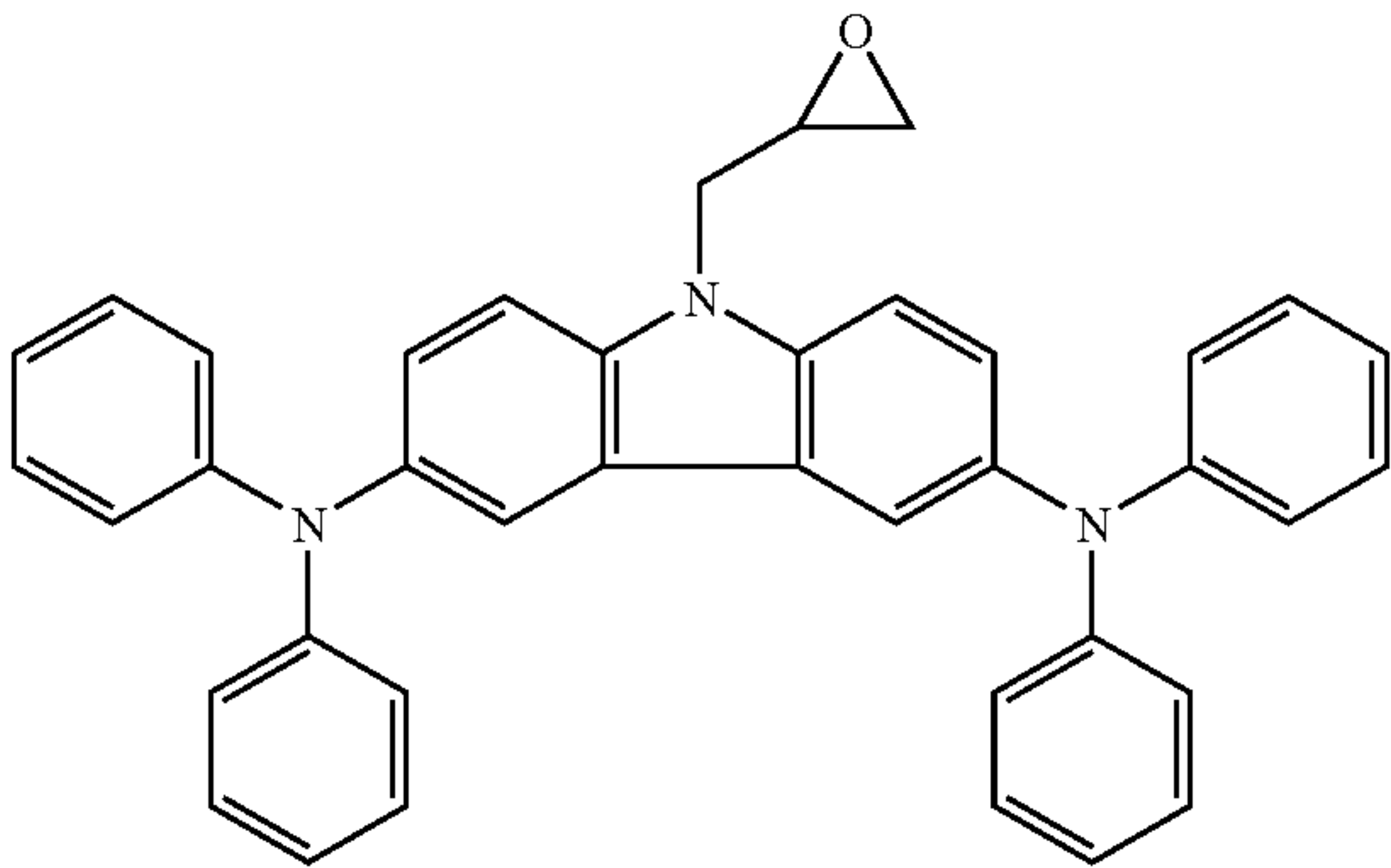


(2)

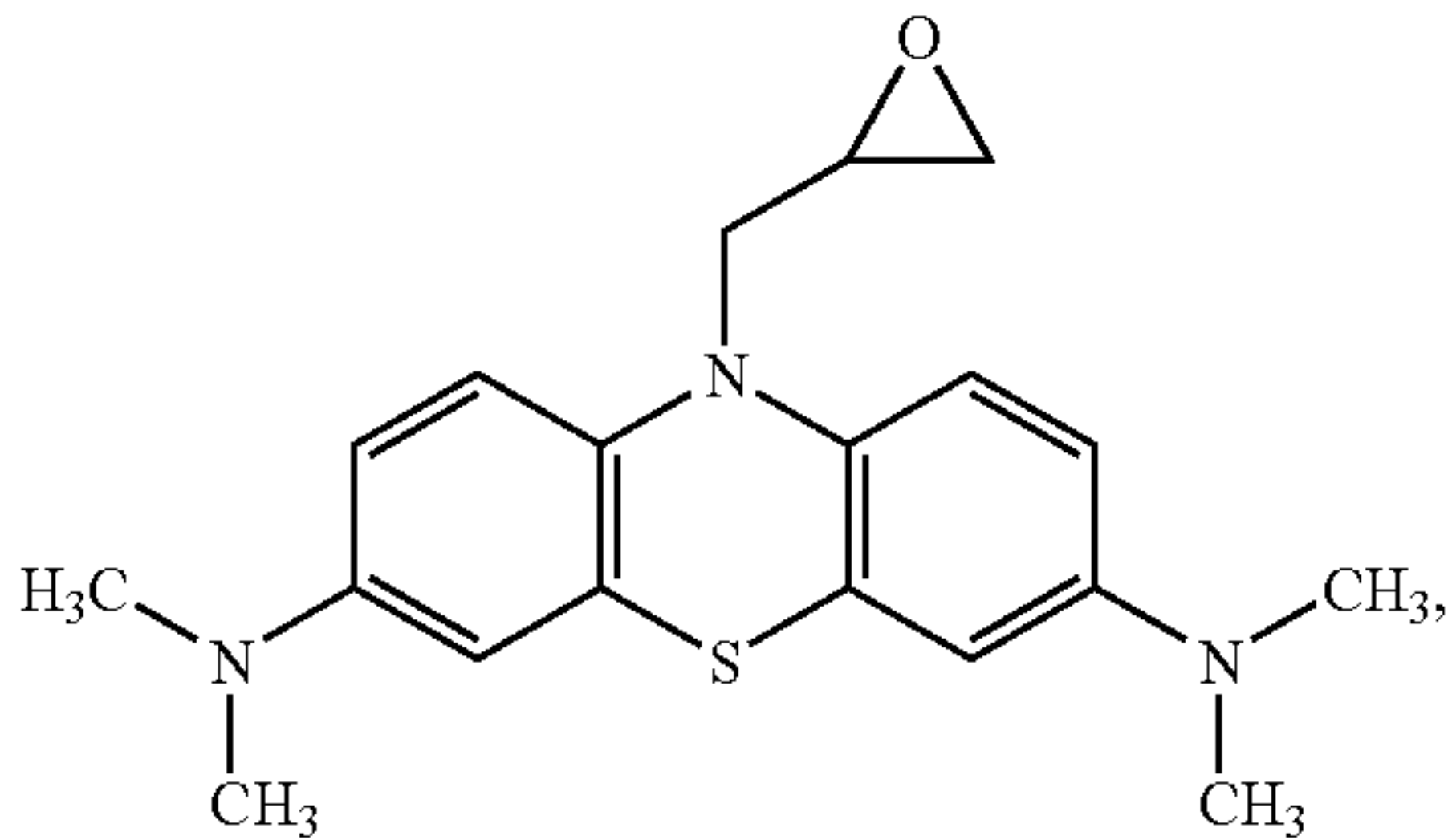
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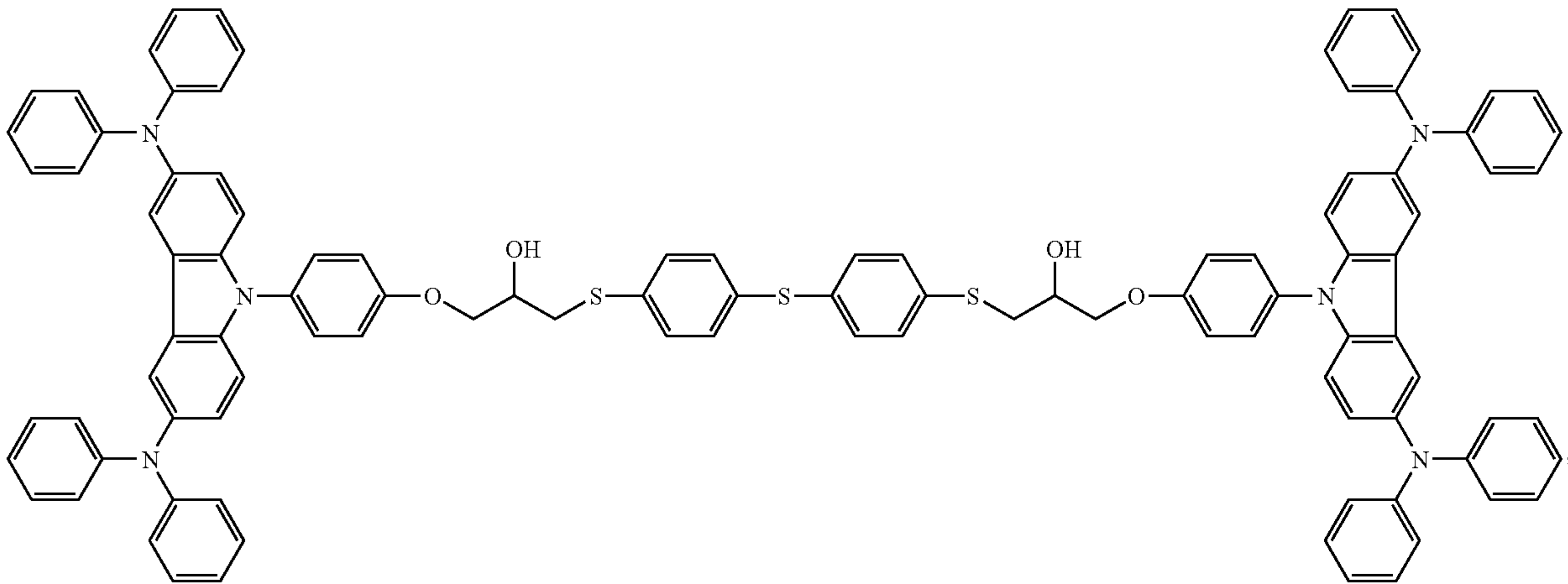


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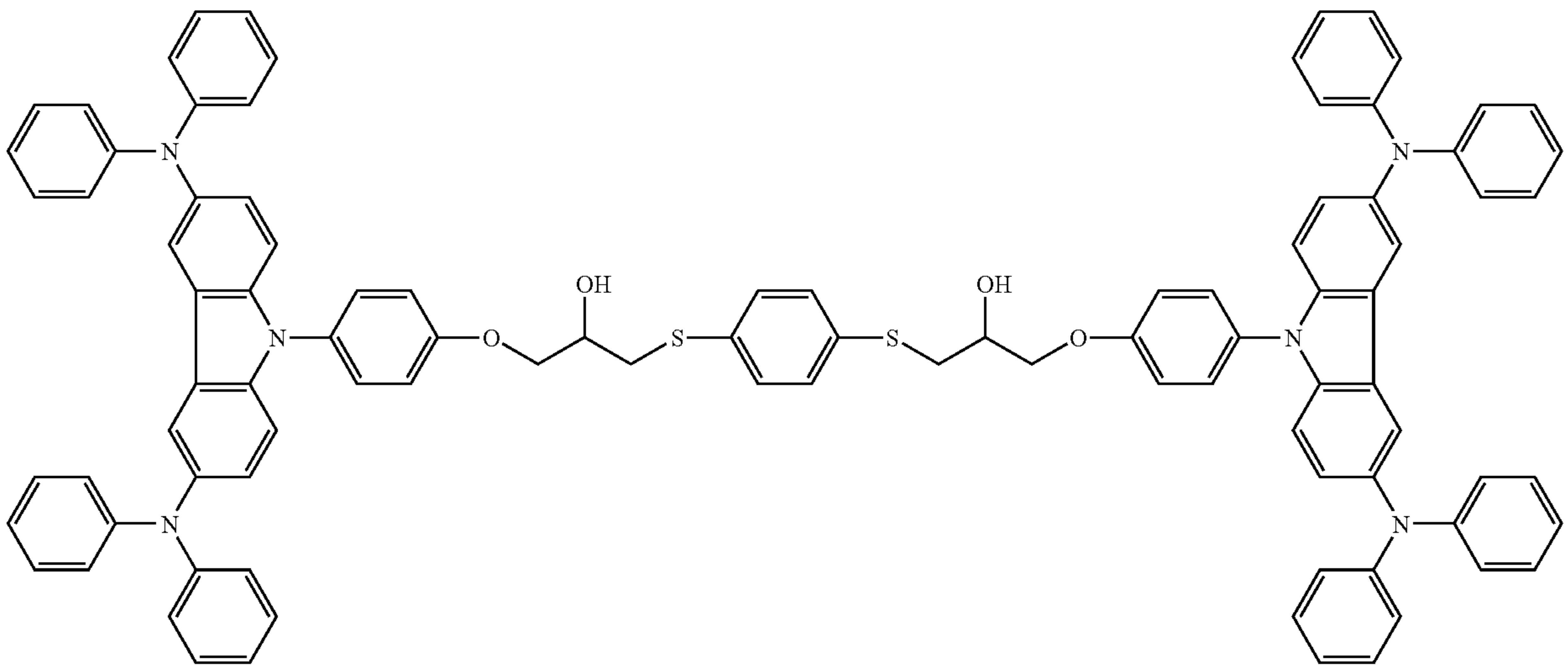
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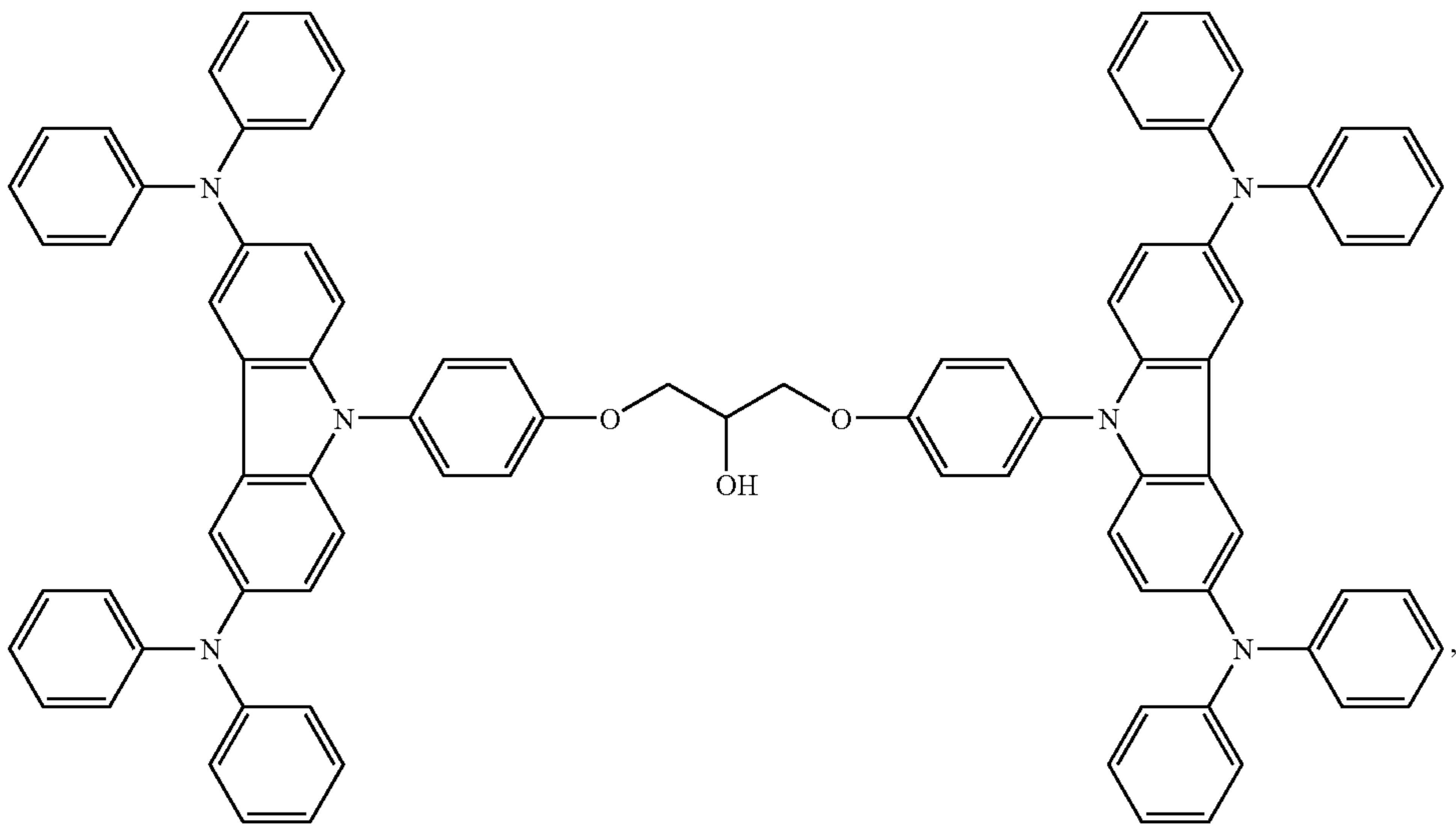
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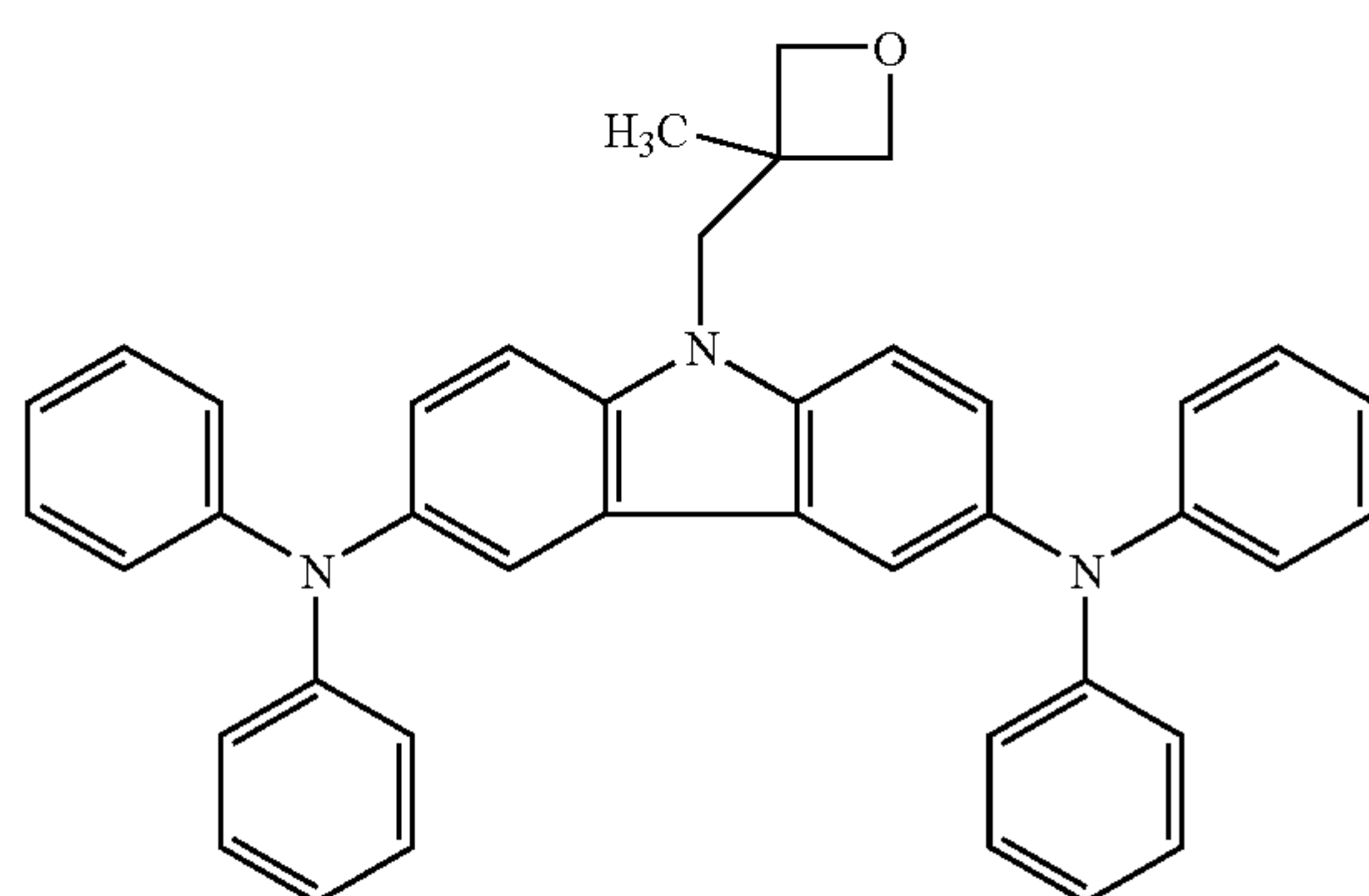
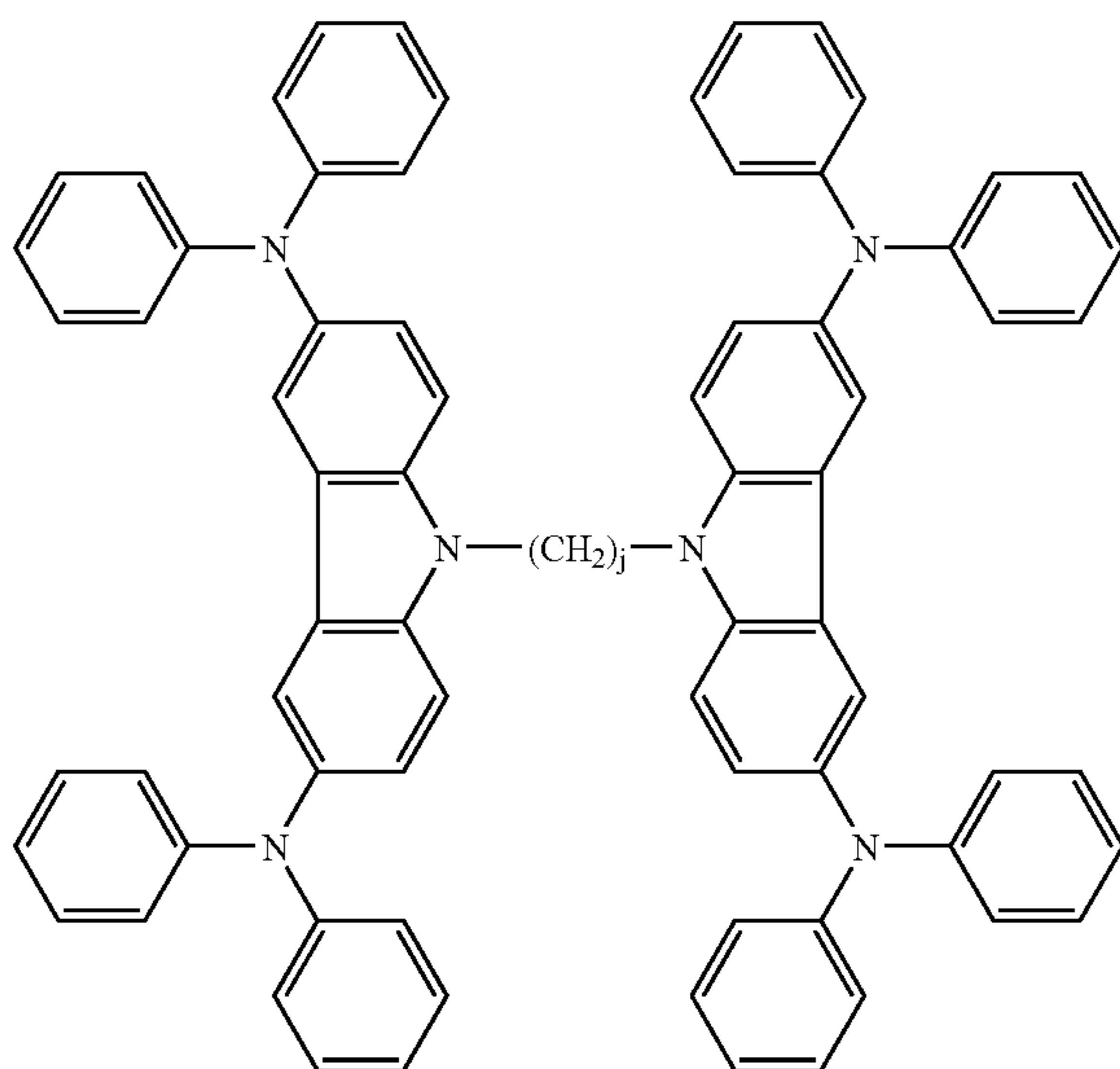
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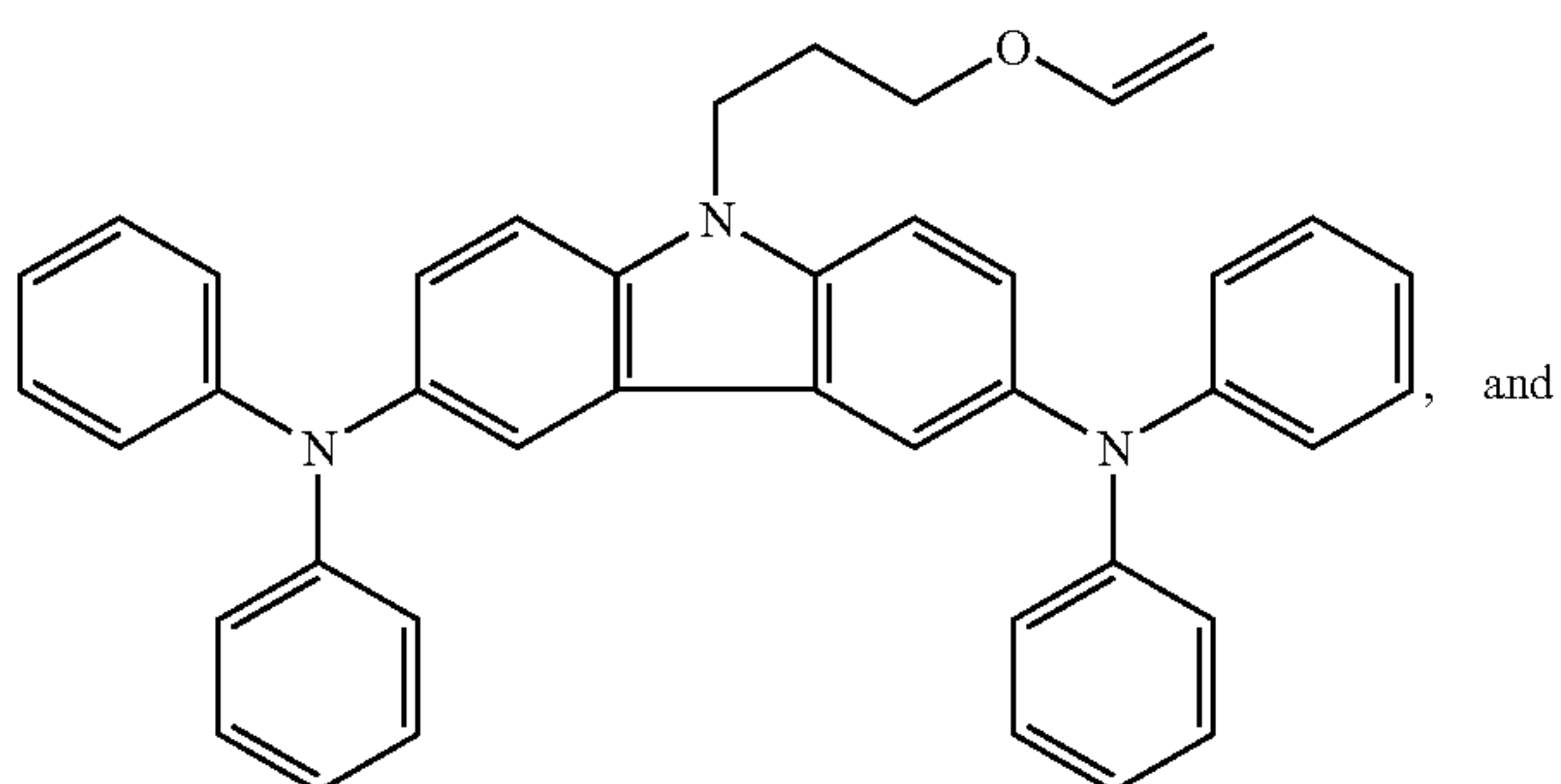
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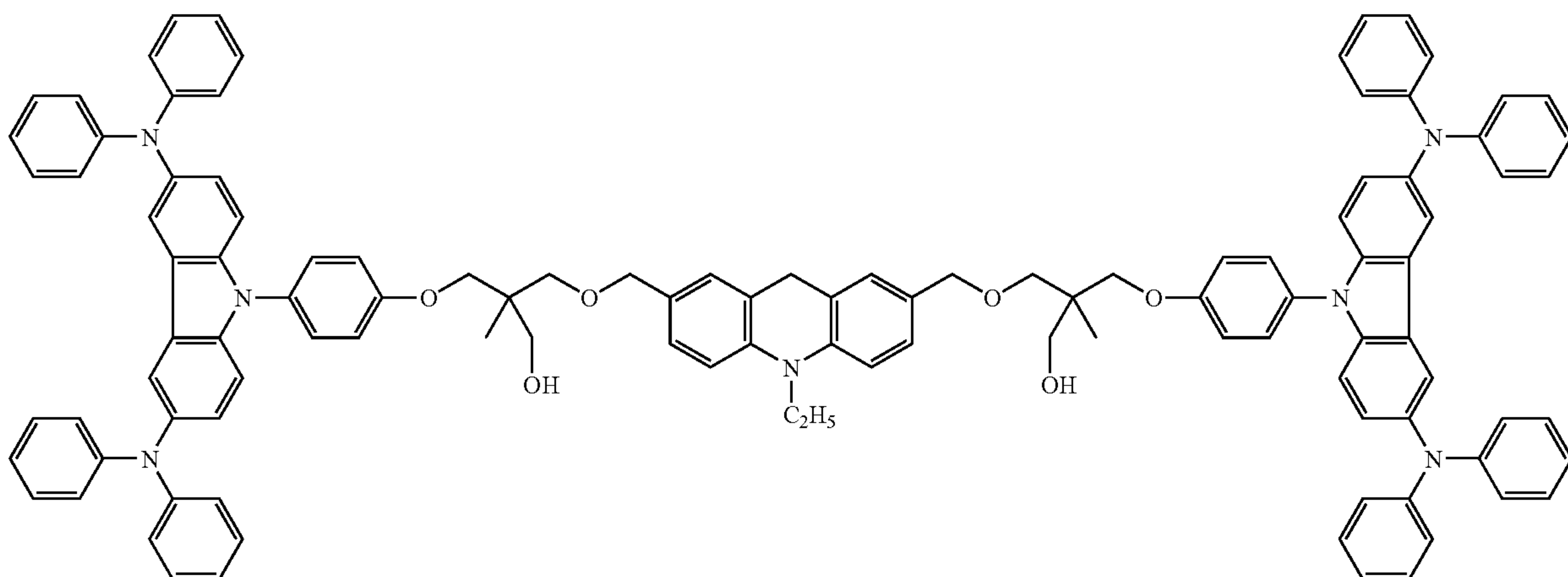


(11)



and

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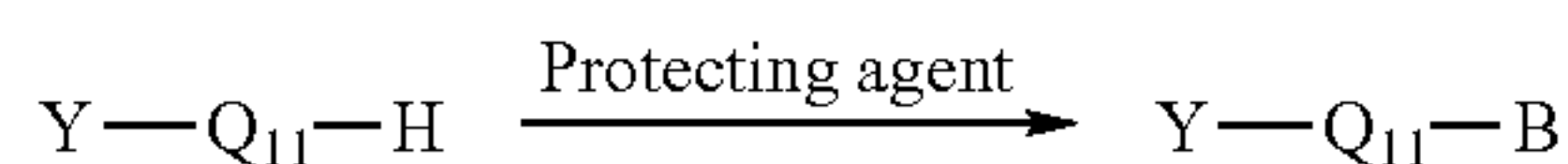


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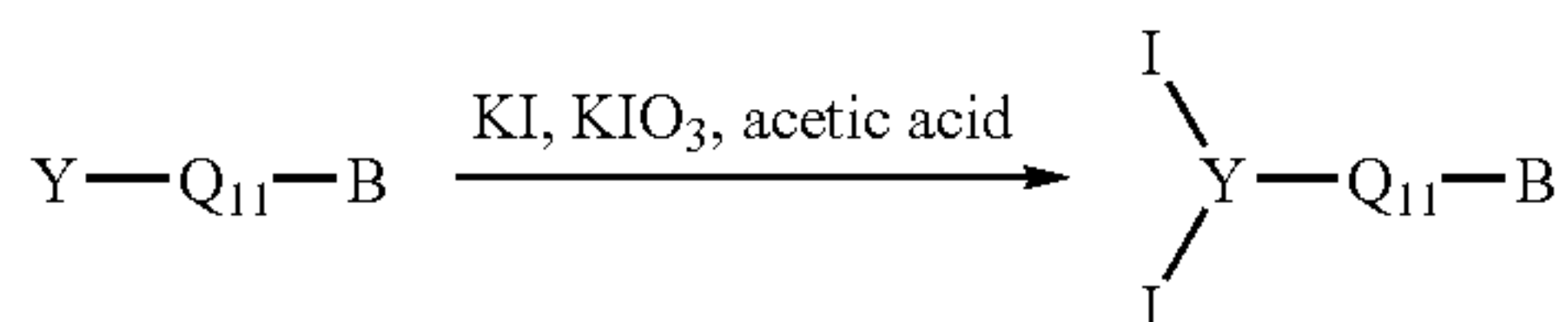
Synthesis Of Charge Transport Materials

The charge transport materials of this invention may be prepared by one of the following multi-step synthetic procedures, although other suitable procedures can be used by a person of ordinary skill in the art based on the disclosure herein.

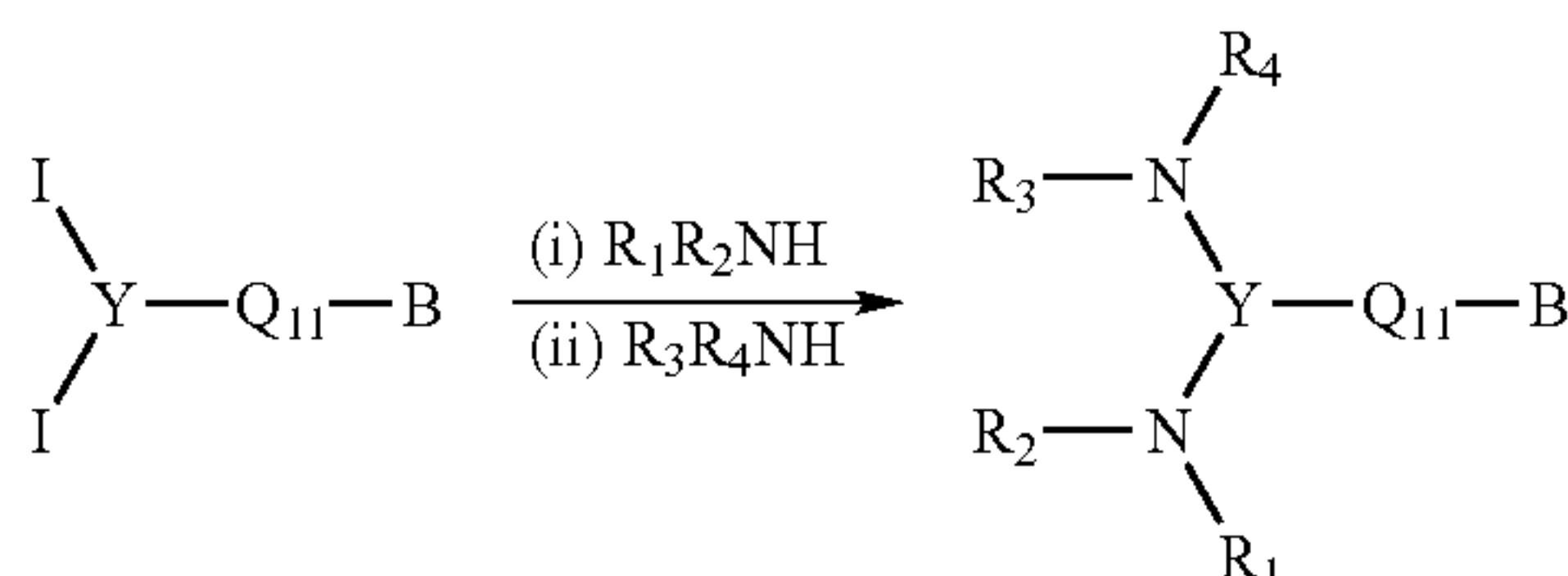
General Synthetic Procedure A for Charge Transport Materials of Formula (I)



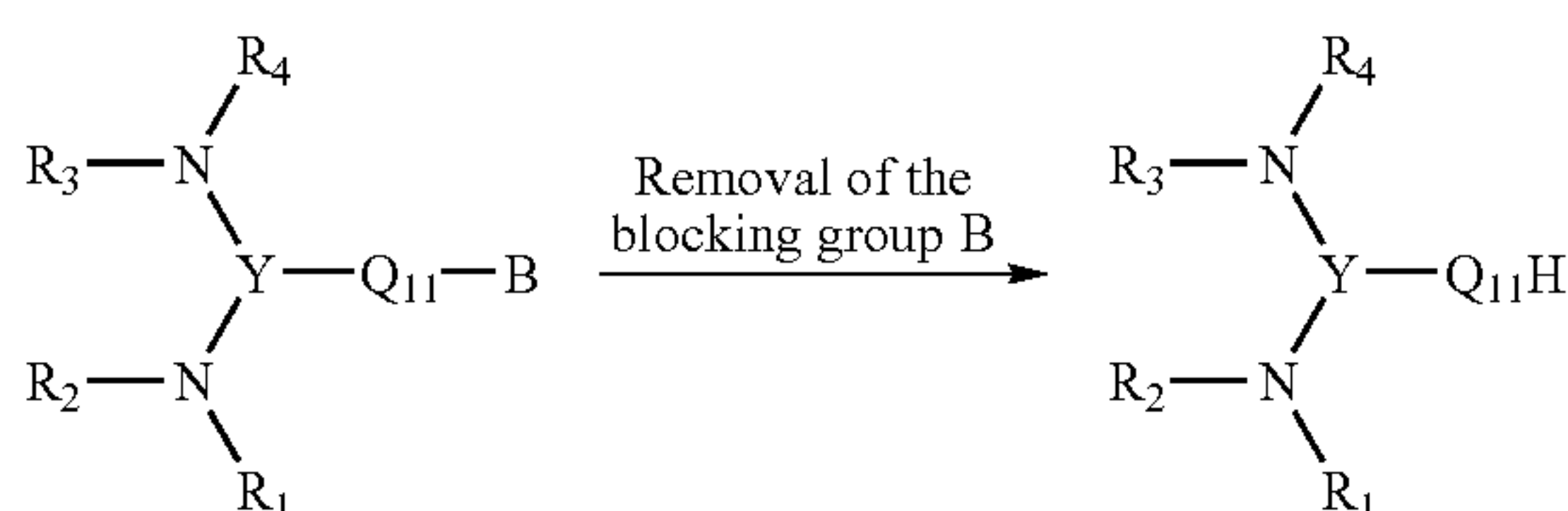
Formula (V)



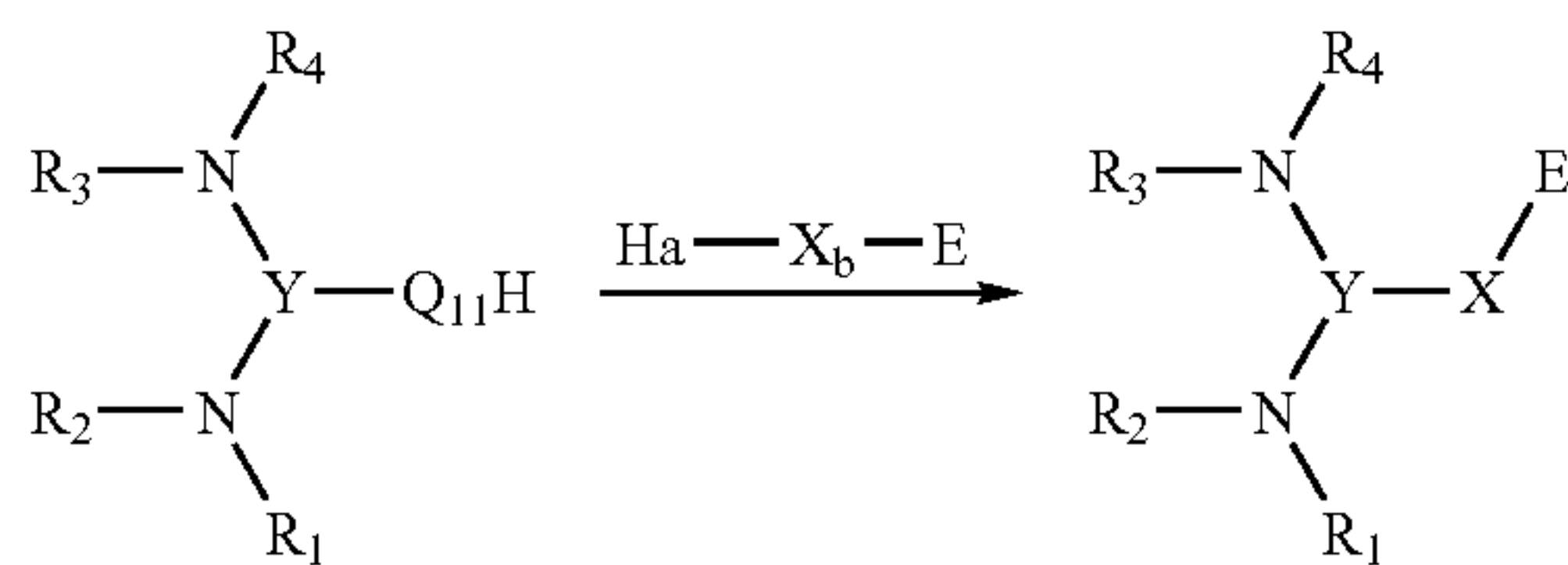
Formula (IV)



Formula (IB)



Formula (I)



The diamino-aromatic heterocyclic compound of Formula (I) may be prepared by the reaction of diamino-aromatic heterocyclic compound of Formula (IB) with an organic halide with a reactive ring group having the formula $Ha-X_b-E$ where Ha is a halide group such as fluoride, chloride, bromide, and iodide; E comprises a reactive ring group, such as an epoxy group, a thiiranyl group, an aziridinyl group, and an oxetanyl group, a reactive functional group, such as a hydroxyl group, a thiol group, a carboxyl group, and an amino group, or an ethylenically unsaturated group, such as a vinyl ether group, an alkene group, acrylate group, a methacrylate group, an acrylamide group, and a methacrylamide group. Formula (IB) is equivalent to Formula (I) having X as a bond and E as a reactive functional group (i.e., $Q_{11}H$) such as a hydroxyl group, a thiol group, an amino group, or a carboxyl group). The $Q_{11}H$ group in Formula (IB) react with $Ha-X_b-E$ to form $Q_{11}-X_b-E$ where the $Q_{11}-X_b$ group is equivalent to the linking group X in Formula (I)

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where $Q_{11}-X_b$ is a $-(CH_2)_n-$ group, where n is an integer between 1 and 20, inclusive, and at least one of the methylene groups, including one of the methylene end groups, is replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group, a BR_g group, or a $P(=O)R_h$ group, where $R_a, R_b, R_c, R_d, R_e, R_f, R_g,$ and R_h are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an acyl group, an alkoxy group, an alkylsulfanyl group, an alkenyl group, such as a vinyl group, an allyl group, and a 2-phenylethenyl group, an alkynyl group, a heterocyclic group, an aromatic group, a part of a ring group, such as cycloalkyl groups, heterocyclic groups, and a benzo group, or an alkyl group where one or more of the hydrogens of the alkyl group is optionally replaced by an aromatic group, a hydroxyl group, a thiol group, a carboxyl group, an amino group, or a halogen. The reaction may be carried out in the presence of a base, such as organic amines and inorganic bases (e.g., potassium hydroxide, sodium hydride, and lithium aluminum hydride).

The reactive ring group may be selected from the group consisting of heterocyclic ring groups that have a higher strain energy than their corresponding open-ring structures. The conventional definition of strain energy is that it represents the difference in energy between the actual molecule and a completely strain-free molecule of the same constitution. More information about the origin of strain energy can be found in the article by Wiberg et al., "A Theoretical Analysis of Hydrocarbon Properties: II Additivity of Group Properties and the Origin of Strain Energy," *J. Am. Chem. Soc.* 109, 985 (1987), which is incorporated herein by reference. The heterocyclic ring group may have 3, 4, 5, 7, 8, 9, 10, 11, or 12 members, in further embodiments 3, 4, 5, 7, or 8 members, in some embodiments 3, 4, or 8 members, and in additional embodiments 3 or 4 members. Non-limiting examples of such heterocyclic ring are cyclic ethers (e.g., epoxides and oxetane), cyclic amines (e.g., aziridine), cyclic sulfides (e.g., thiirane), cyclic amides (e.g., 2-azetidinone, 2-pyrrolidone, 2-piperidone, caprolactam, enantholactam, and capryllactam), N-carboxy- α -amino acid anhydrides, lactones, and cyclosiloxanes. The chemistry of the above heterocyclic rings is described in George Odian, "Principle of Polymerization," second edition, Chapter 7, p. 508-552 (1981), which is incorporated herein by reference.

The preparations of some charge transport materials having a reactive ring group have been disclosed in U.S. patent application Ser. Nos. 10/749,178, 10/695,581, 10/692,389, 10/634,164, 10/663,970, 10/749,164, 10/772,068, 10/749,269, and 10/758,869, all of which are incorporated herein by reference. In general, the aromatic compound having a reactive ring group may be prepared by the reaction of the corresponding aromatic compound having a hydroxyl group, thiol group, a carboxyl group, a primary amino group, or a secondary amine group with an organic halide with a reactive ring group.

In some embodiments of interest, the reactive ring group is an epoxy group. A diamino-aromatic heterocyclic compound having an epoxy group may be prepared by reacting a corresponding compound with an organic halide comprising an epoxy group. Non-limiting examples of suitable

organic halide comprising an epoxy group as the reactive ring group are epihalohydrins, such as epichlorohydrin. The organic halide comprising an epoxy group can also be prepared by the epoxidation reaction of the corresponding alkene having a halide group. Such epoxidation reaction is described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 494-498, incorporated herein by reference. The alkene having a halide group can be prepared by the Wittig reaction between a suitable aldehyde or keto compound and a suitable Wittig reagent. The Wittig and related reactions are described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 69-77, which is incorporated herein by reference.

In other embodiments of interest, the reactive ring group is a thiiranyl group. A diamino-aromatic heterocyclic compound having an epoxy group, such as those described above, can be converted into the corresponding thiiranyl compound by refluxing the epoxy compound and ammonium thiocyanate in tetrahydrofuran. Alternatively, the corresponding thiiranyl compound may be obtained by passing a solution of the above-described epoxy compound through 3-(thiocyano)propyl-functionalized silica gel (commercially available from Aldrich, Milwaukee, Wis.). Alternatively, a thiiranyl compound may be obtained by the thia-Payne rearrangement of a corresponding epoxy compound. The thia-Payne rearrangement is described in Rayner, C. M. Synlett 1997, 11; Liu, Q. Y.; Marchington, A. P.; Rayner, C. M. Tetrahedron 1997, 53, 15729; Ibuka, T. Chem. Soc. Rev. 1998, 27, 145; and Rayner, C. M. Contemporary Organic Synthesis 1996, 3, 499. All the above four articles are incorporated herein by reference.

In other embodiments of interest, the reactive ring group is an aziridiny group. An aziridine compound may be obtained by the aza-Payne rearrangement of a corresponding diamino-aromatic heterocyclic compound having an epoxy group, such as one of those epoxy compounds described above. The thia-Payne rearrangement is described in Rayner, C. M. Synlett 1997, 11; Liu, Q. Y.; Marchington, A. P.; Rayner, C. M. Tetrahedron 1997, 53, 15729; and Ibuka, T. Chem. Soc. Rev. 1998, 27, 145. All the above three articles are incorporated herein by reference. Alternatively, an aziridine compound may be prepared by the addition reaction between a suitable nitrene compound and a suitable alkene. Such addition reaction is described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 446-448, incorporated herein by reference.

In further embodiments of interest, the reactive ring group is an oxetanyl group. An oxetane compound may be prepared by the Paterno-Buchi reaction between a suitable carbonyl compound and a suitable alkene. The Paterno-Buchi reaction is described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 335-336, which is incorporated herein by reference. 3-Chloromethyl-3-alkyloxetanes may be prepared according to the procedure disclosed in Japanese Publication No. 10-212282, which is incorporated herein by reference.

In additional examples, the reactive ring may be a 5 or 7-membered ring comprising a —COO— group or a —CONR— group, such as butyrolactone, N-methylbutyrolactam, N-methylcaprolactam, and caprolactone.

The diamino-aromatic heterocyclic compound of Formula (IB) may be prepared by the following multi-step procedure. The first step is the reaction between an aromatic heterocyclic compound having the formula $\text{Y-Q}_{11}\text{H}$ where Y comprises an aromatic heterocyclic group and Q_{11}H comprises a reactive functional group such as a hydroxyl group, a thiol group, a carboxyl group, and an amino group, with a protecting agent to form the product, $\text{Y-Q}_{11}\text{-B}$, and to protect the Q_{11}H group for subsequent reactions.

Non-limiting examples of the protecting group for amino groups include an acyl group (e.g., formyl and its derivatives, acetyl and its derivatives, benzoyl and its derivatives, and diacyl and its derivatives), an urea group, an urethane group, an alkyl group, an aryl group, an azomethine group, an 1,3-dicarbonyl group, an N-nitroso group, an N-nitro group, a phosphoryl group, a sulfenyl group, a sulfonyl group, an N-sulfonic acid group, and a trialkylsilyl group. The protection of amino groups and the removal of the amino protecting groups are described in J. F. W. McOmie, "Protective Groups in Organic Chemistry," chapter 2, Plenum Press (1973), which is incorporated herein by reference.

Non-limiting examples of the protecting group for the alcoholic hydroxyl groups include an ether group, an acetal group, a ketal group, and an ester group. Non-limiting examples of the protecting group for the phenolic hydroxyl groups include an alkyl group and an acyl group. The protection of the hydroxyl group and the removal of the hydroxyl protecting groups are described in J. F. W. McOmie, "Protective Groups in Organic Chemistry," chapters 3-4, Plenum Press (1973), which is incorporated herein by reference.

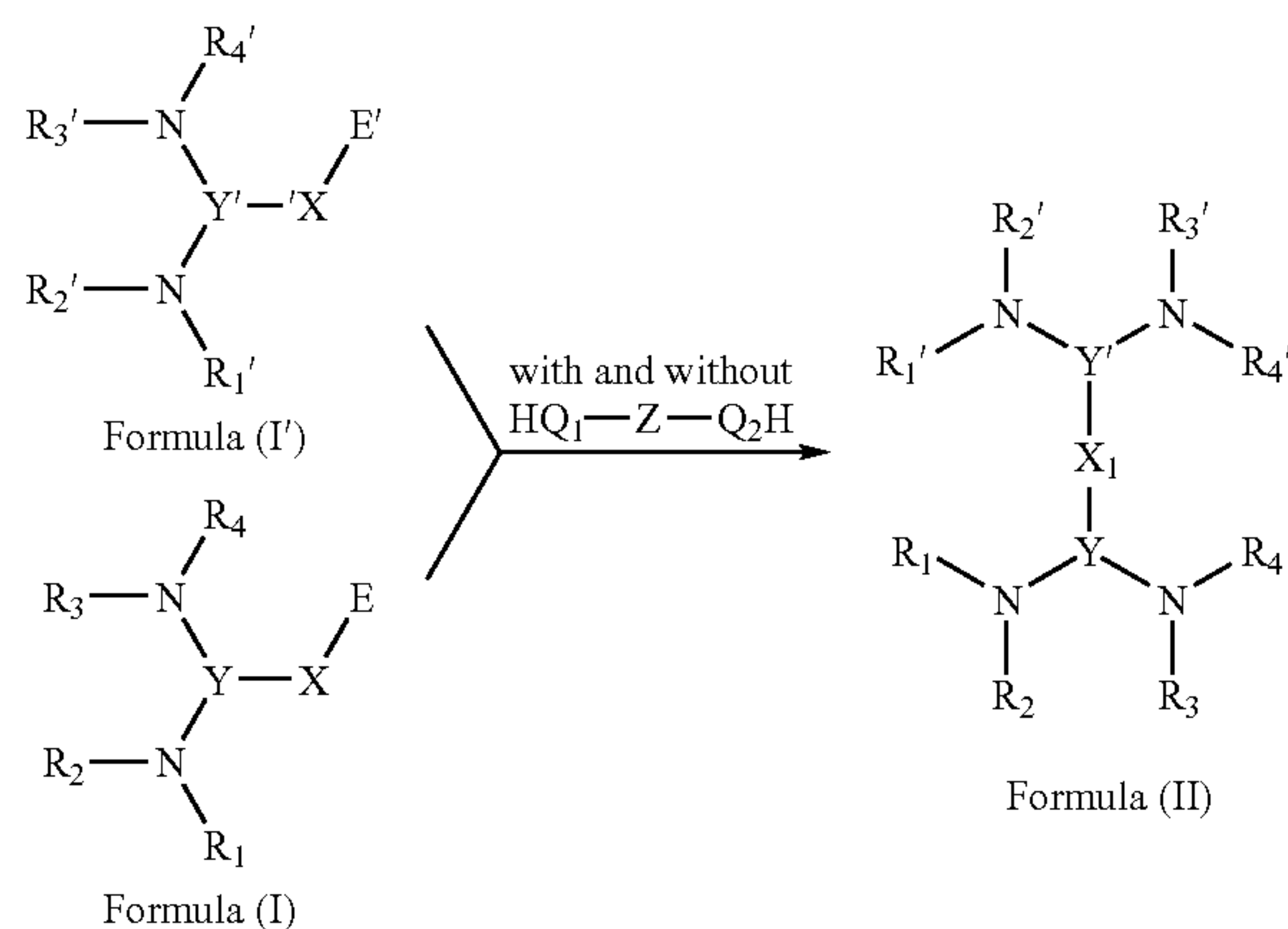
Non-limiting examples of the protecting group for the carboxyl group include ester groups. The protection of the carboxyl group and the removal of the carboxyl protecting groups are described in J. F. W. McOmie, "Protective Groups in Organic Chemistry," chapter 5, Plenum Press (1973), which is incorporated herein by reference.

Non-limiting examples of the protecting group for the thiol group include a thioether group, a monothioacetal group, a dithioacetal group, a thiazolidinyl group, a thiol ester group, and a sulfenyl group. The protection of the thiol group and the removal of the thiol protecting groups are described in J. F. W. McOmie, "Protective Groups in Organic Chemistry," chapter 7, Plenum Press (1973), which is incorporated herein by reference.

The compound $\text{Y-Q}_{11}\text{-B}$ may react with a mixture of potassium iodide, potassium iodate, and acetic acid to form the diiodo compound of Formula (V) at an elevated temperature. The compound of Formula (IV) may be prepared by refluxing in o-dichlorobenzene under nitrogen the diiodo compound of Formula (V) with one or two amine compounds, simultaneously or sequentially, in the presence of a mixture of powdered potassium carbonate, copper powder, and 18-crown-6. The amine $\text{R}_1\text{R}_2\text{NH}$ and the amine $\text{R}_3\text{R}_4\text{NH}$ may be the same or different. The diamino-aromatic heterocyclic compound of Formula (IB) may be prepared by removing the protecting group B in the compound of Formula (IV) by one of the removal methods as described in J. F. W. McOmie, "Protective Groups in Organic Chemistry," Chapters 2-5, and 7, Plenum Press (1973), which is incorporated herein by reference. The desired product may be isolated and purified by the conventional purification techniques such as column chromatography and recrystallization.

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General Synthetic Procedure B for Bridged Charge Transport Materials of Formula (II)



In some embodiments, the bridged charge transport materials of Formula (II) may be prepared by reacting a bridging compound having the formula HQ_1-Z-Q_2H with a compound of Formula (I) and a compound of Formula (I') either simultaneously or sequentially, where Y and Y' comprise, each independently, an aromatic heterocyclic group; X , X' , and Z comprise, each independently, a bond or a linking group; E and E' comprise, each independently, a reactive ring group, such as an epoxy group, a thiranyl group, an aziridinyl group, and an oxetanyl group, or a reactive functional group, such as a hydroxyl group, a thiol group, a carboxyl group, and an amino group; Q_1 and Q_2 are, each independently, O, S, and NR; and R , R_1 , R_2 , R_3 , R_4 , R_1' , R_2' , R_3' , and R_4' comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group. The reaction may be catalyzed by an organic base such as triethylamine.

The compound of Formula (I) and the compound of Formula (I') may be the same or different. The bridged charge transport materials of Formula (II) are symmetrical if the compound of Formula (I) and the compound of Formula (I') are the same and HQ_1-Z-Q_2H is symmetrical. The bridged charge transport materials of Formula (II) are unsymmetrical if the compound of Formula (I) and the compound of Formula (I') are different or HQ_1-Z-Q_2H is unsymmetrical. When Formula (I) is the same as Formula (I'), the bridging compound may react with Formula (I) and Formula (I') in one step. When Formula (I) is different than Formula (I'), the bridging compound may react with Formula (I) and Formula (I') sequentially. In further embodiments, X , X' , and Z comprise, each independently, a $-(CH_2)_m-$ group, where m is an integer between 1 and 20, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, $C=O$, $O=S=O$, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group, a BR_g group, or a $P(=O)R_h$ group, where R_a , R_b , R_c , R_d , R_e , R_f , R_g , and R_h are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an acyl group, an alkoxy group, an alkylsulfanyl group, an alkenyl group, such as a vinyl group, an allyl group, and a 2-phenylethenyl group, an alkynyl group, a heterocyclic group, an aromatic group, a part of a ring group, such as cycloalkyl groups, heterocyclic groups, and a benzo group, or an alkyl group where one or more of the hydrogens of the alkyl group

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is optionally replaced by an aromatic group, a hydroxyl group, a thiol group, a carboxyl group, an amino group, or a halogen.

In other embodiments, the bridging compound may be a diol, a dithiol, a diamine, a dicarboxylic acid, a hydroxylamine, an amino acid, a hydroxyl acid, a thiol acid, a hydroxythiol, or a thioamine. Non-limiting examples of suitable dithiol are 3,6-dioxa-1,8-octanedithiol, erythro-1,4-dimercapto-2,3-butanediol, (\pm)-threo-1,4-dimercapto-2,3-butanediol, 4,4'-thiobisbenzenethiol, 1,4-benzenedithiol, 1,3-benzenedithiol, sulfonyl-bis(benzenethiol), 2,5-dimercapto-1,3,4-thiadiazole, 1,2-ethanedithiol, 1,3-propanedithiol, 1,4-butanedithiol, 2,3-butanedithiol, 1,5-pentanedithiol, and 1,6-hexanedithiol. Non-limiting examples of suitable diols are 2,2'-bi-7-naphthol, 1,4-dihydroxybenzene, 1,3-dihydroxybenzene, 10,10-bis(4-hydroxyphenyl)anthrone, 4,4'-sulfonyldiphenol, bisphenol, 4,4'-(9-fluorenylidene)diphenol, 1,10-decanediol, 1,5-pentanediol, diethylene glycol, 4,4'-(9-fluorenylidene)-bis(2-phenoxyethanol), bis(2-hydroxyethyl)terephthalate, bis[4-(2-hydroxyethoxy)phenyl] sulfone, hydroquinone-bis(2-hydroxyethyl)ether, and bis(2-hydroxyethyl)piperazine. Non-limiting examples of suitable diamine are diaminoarenes, and diaminoalkanes. Non-limiting examples of suitable dicarboxylic acid are phthalic acid, terephthalic acid, adipic acid, and 4,4'-biphenyldicarboxylic acid. Non-limiting examples of suitable hydroxylamine are p-aminophenol and fluoresceinamine. Non-limiting examples of suitable amino acid are 4-aminobutyric acid, phenylalanine, and 4-aminobenzoic acid. Non-limiting examples of suitable hydroxyl acid are salicylic acid, 4-hydroxybutyric acid, and 4-hydroxybenzoic acid. Non-limiting examples of suitable hydroxythiol are monothiohydroquinone and 4-mercapto-1-butanol. Non-limiting example of suitable thioamine is p-aminobenzenethiol. Non-limiting example of suitable thiol acid are 4-mercaptobenzoic acid and 4-mercaptobutyric acid. Almost all of the above bridging compounds are available commercially from Aldrich and other chemical suppliers.

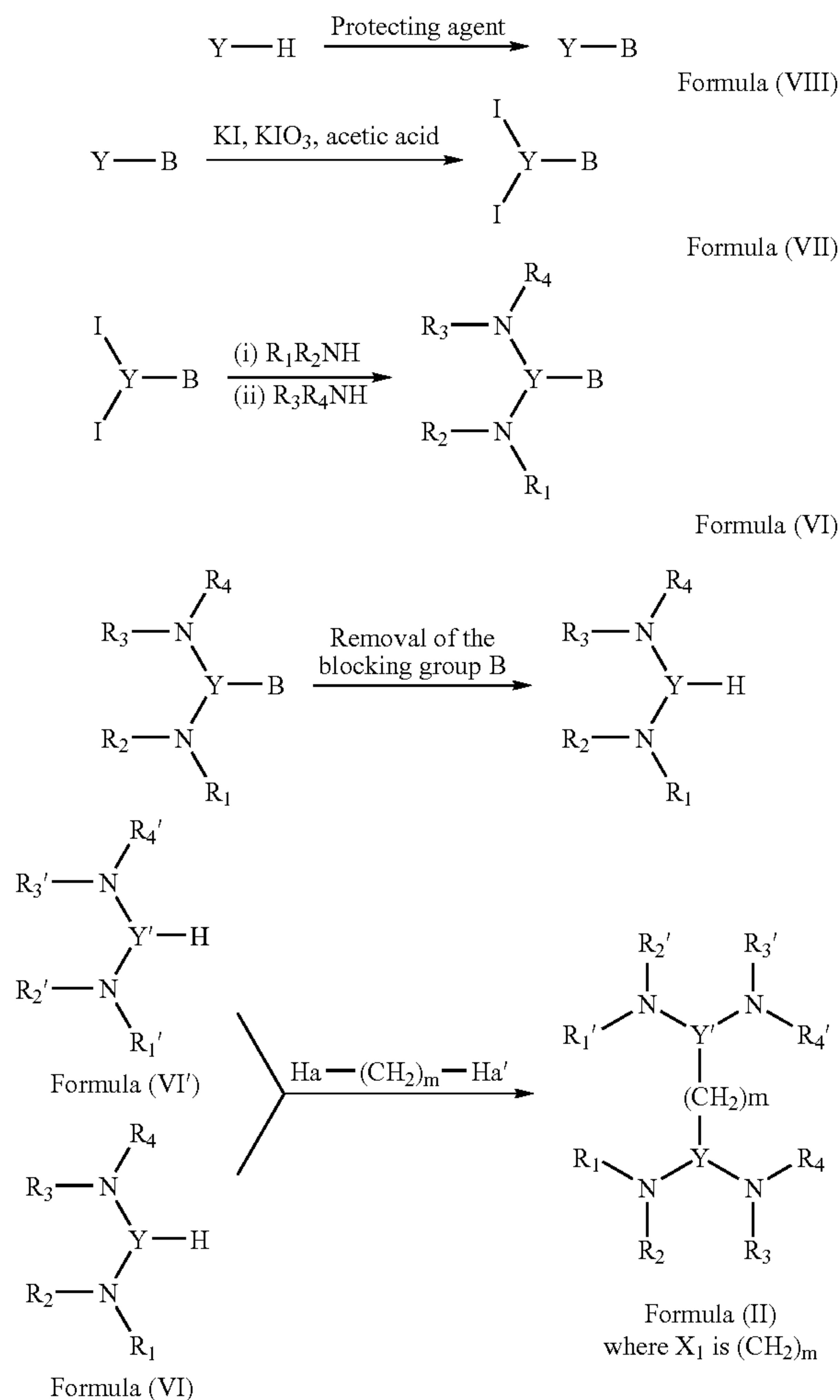
In other embodiments, the bridged charge transport materials of Formula (II) may be prepared by reacting a compound of Formula (I) with a compound of Formula (I') where Y and Y' comprise, each independently, an aromatic heterocyclic group; X and X' comprise, each independently, a bond or a linking group; E comprises a reactive ring group (or a reactive functional group); E' comprises a reactive functional group (or a reactive ring group); and R_1 , R_2 , R_3 , R_4 , R_1' , R_2' , R_3' , and R_4' comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group. The reaction may be catalyzed by an organic base such as triethylamine.

In further embodiments, X and X' comprise, each independently, a $-(CH_2)_m-$ group, where m is an integer between 1 and 20, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, $C=O$, $O=S=O$, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group, a BR_g group, or a $P(=O)R_h$ group, where R_a , R_b , R_c , R_d , R_e , R_f , R_g , and R_h are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an acyl group, an alkoxy group, an alkylsulfanyl group, an alkenyl group, such as a vinyl group, an allyl group, and a 2-phenylethenyl group, an alkynyl group, a heterocyclic group, an aromatic group, a part of a ring group, such as cycloalkyl groups, heterocyclic groups, and a benzo group, or an alkyl group where one or more of

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the hydrogens of the alkyl group is optionally replaced by an aromatic group, a hydroxyl group, a thiol group, a carboxyl group, an amino group, or a halogen.

General Synthetic Procedure C for Bridged Charge Transport Materials of Formula (II)



Alternatively, the bridged charge transport materials of Formula (II) where X_1 comprises an alkylene group having the formula $-(CH_2)_m-$ may be prepared by reacting a bridging compound having the formula $Ha-(CH_2)_m-Ha'$ with a diamino-aromatic heterocyclic compound of Formula (VI) and a diamino-aromatic heterocyclic compound of Formula (VI') where Y and Y' comprise, each independently, an N—H containing aromatic heterocyclic group, such as pyrrolyl, indolyl, and carbazoyl, $R_1, R_2, R_3, R_4, R_1', R_2', R_3',$ and R_4' comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, and Ha and Ha' comprise, each independently, a halide group, such as chloride, bromide, and iodide. The reaction may be catalyzed by benzyltrimethylammonium chloride or an organic base such as triethylamine.

The compound of Formula (VI) and the compound of Formula (VI') may be the same or different. The bridged charge transport materials of Formula (II) are symmetrical if the compound of Formula (VI) and the compound of Formula (VI') are the same. The bridged charge transport

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materials of Formula (II) are unsymmetrical if the compound of Formula (VI) and the compound of Formula (VI') are different. When Formula (VI) is the same as Formula (VI'), the bridging compound may react with Formula (VI) and Formula (VI') in one step. When Formula (VI) is different than Formula (VI'), the bridging compound may react with Formula (VI) and Formula (VI') sequentially.

The diamino-aromatic heterocyclic compounds of Formula (VI) and (VI') may be prepared by the following multi-step procedure. The first step is the reaction between an N—H containing aromatic heterocyclic compound, such as pyrroles, indoles, and carbazoles, having the formula Y—H where Y comprises an N—H containing aromatic heterocyclic group, such as pyrrolyl, indolyl, and carbazoyl, with a protecting agent to form the product, Y—B, and to protect the N—H group for subsequent reactions.

Non-limiting examples of the protecting group for the N—H group include an acyl group (e.g., formyl and its derivatives, acetyl and its derivatives, benzoyl and its derivatives, and diacyl and its derivatives), an urea group, an urethane group, an alkyl group, an aryl group, an azomethine group, an 1,3-dicarbonyl group, an N-nitroso group, an N-nitro group, a phosphoryl group, a sulfenyl group, a sulfonyl group, an N-sulfonic acid group, and a trialkylsilyl group. The protection of amino groups and the removal of the amino protecting groups are described in J. F. W. McOmie, "Protective Groups in Organic Chemistry," chapter 2, Plenum Press (1973), which is incorporated herein by reference.

The compound Y—B may react with a mixture of potassium iodide, potassium iodate, and acetic acid to form the diiodo compound of Formula (VIII) at an elevated temperature. The diamino-aromatic heterocyclic compounds of Formula (VII) may be prepared by refluxing in o-dichlorobenzene under nitrogen the diiodo compound of Formula (VIII) with one or two amine compounds, simultaneously or sequentially, in the presence of a mixture of powdered potassium carbonate, copper powder, and 18-crown-6. The amine R_1R_2NH and the amine R_3R_4NH may be the same or different. The diamino-aromatic heterocyclic compound of Formula (VI) or (VI') may be prepared by removing the protecting group B in the diamino-aromatic heterocyclic compounds of Formula (VII) by one of the removal methods as described in J. F. W. McOmie, "Protective Groups in Organic Chemistry," Chapters 2-5, and 7, Plenum Press (1973), which is incorporated herein by reference. The desired product may be isolated and purified by the conventional purification techniques such as column chromatography and recrystallization.

In general, a person of ordinary skill in the art can replace the reactive ring group, with a first functional group, such as a carboxylic acid group and an acid anhydride group, that can react with HQ_1-Z-Q_2H where Q_1H and Q_2H are, each independently, an amino group. Similarly, the E group in Formula (I) may comprise a carbonyl group and the Q_1H and Q_2H groups in HQ_1-Z-Q_2H can be replaced with a second functional group and a third functional group respectively, both of which can react with the carbonyl group. The second functional group and the third functional group may be the same or different. Non-limiting examples of the second functional group and the third functional group include a hydroxyl group, a thiol group, and an amino group. Furthermore, a person of ordinary skill in the art can replace both the E group of Formula (I) and the E' group of Formula (I') with a fourth functional group and a fifth functional group where the fourth functional group is reactive toward the fifth functional group.

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The invention will now be described further by way of the following examples.

EXAMPLES

Example 1

Synthesis of Charge Transport Materials

This example describes the synthesis and characterization of Compounds (1)-(12) in which the numbers refer to formula numbers above. The characterization involves chemical characterization of the compositions. The electrostatic characterization, such as mobility and ionization potential, of the materials formed with the compositions is presented in a subsequent example.

Compound (1)

9-(4-Methoxyphenyl)carbazole. A mixture of 9H-carbazole (5.51 g, 33 mmol, available from Aldrich, Milwaukee, Wis.), 4-iodoanisole (10 g, 43 mmol, available from Aldrich), powdered potassium carbonate (36.43 g, 264 mmol), copper powder (8.38 g, 132 mmol) and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane, 0.56 g, 2.1 mmol, obtained from Aldrich) was refluxed in o-dichlorobenzene (30 ml, obtained from Aldrich) under nitrogen for 24 hours. The copper and inorganic salts were filtered. The solvent was removed by distillation. The product, 9-(4-methoxyphenyl)carbazole, was recrystallized, washed with methanol, filtered, and dried. The yield was 8.432 g (93.7%). The ¹H-NMR spectrum (300 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ, ppm): 4.04 (s, 3H, OCH₃), 7.24-7.63 (m, 8H, Ar), 8.35-8.40 (m, 4H, Ar). The ¹³C-NMR spectrum (75.4 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ, ppm): 55.95 (OCH₃), 110.07, 115.44, 120.03, 120.68, 123.53, 126.25, 128.90, 130.65, 141.78, 159.26 (all Ar). The infrared absorption spectrum of the product was characterized by the following the following absorption frequencies (KBr windows, in cm⁻¹): 3040 (C—H Ar), 2900 (C—H Alk), 1250 (C—O—C). The mass spectrum of the product was characterized by the following ions (in m/z): 274 (M⁺).

3,6-Diiodo-9-(4-methoxyphenyl)carbazole. Potassium iodate (16.05 g, 75 mmol, obtained from Aldrich) was added in one portion to a stirred mixture of 9-(4-methoxyphenyl)carbazole (9.54 g, 34 mmol), potassium iodide (10.96 g, 66 mmol), and acetic acid (100 ml) at 80° C. The reaction mixture was stirred and heated for 1 hour. After the reaction was completed, the acetic acid was removed by distillation. The residue was dissolved in ethyl acetate and washed several times with an aqueous solution of sodium bicarbonate. The organic layer was dried over anhydrous magnesium sulfate, filtered, concentrated, and dried. The yield of 3,6-diiodo-9-(4-methoxyphenyl)carbazole was 16.07 g (87.6%). The ¹H-NMR spectrum (100 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ, ppm): 4.04 (s, 3H, OCH₃), 7.24-7.63 (m, 6H, Ar), 8.35-8.40 (m, 4H, Ar). The mass spectrum of the product was characterized by the following ions (in m/z): 525 (M⁺).

3,6-Bis(diphenylamino)-9-(4-methoxyphenyl)carbazole. A mixture of 3,6-diiodo-9-(4-methoxyphenyl)carbazole (3 g, 5.7 mmol), diphenylamine (1.86 g, 11 mmol, obtained from Aldrich), powdered potassium carbonate (6.35 g, 46 mmol), copper powder (1.46 g, 23 mmol), and 18-crown-6 (0.4 g, obtained from Aldrich) was refluxed in o-dichlorobenzene (30 ml) under nitrogen 24 hours. The copper and inorganic salts were filtered. The solvent was removed by

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distillation. The product was recrystallized, washed with methanol, filtered, and dried. The yield of 3,6-bis(diphenylamino)-9-(4-methoxyphenyl)carbazole was 3.25 g (93.7%). The ¹H-NMR spectrum (400 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ, ppm): 3.94 (s, 3H, OCH₃), 7.00-7.40 (m, 26H, Ar), 7.42-7.59 (m, 2H, Ar), 7.90 (s, 2H, Ar). The ¹³C-NMR spectrum (100 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ, ppm): 55.52 (OCH₃), 110.72, 115.04, 118.69, 121.51, 122.61, 123.67, 125.89, 128.3, 128.98, 138.88, 140.24, 148.46, 154.87 (all Ar).

A solution of sodium ethanethiolate was prepared by adding ethanethiol (0.55 ml, 7.5 mmol, obtained from Aldrich) to a suspension of sodium hydride (0.15 g, 5 mmol, 60% dispersion in mineral oil, available from Aldrich) in 10 ml of dry dimethylformamide (DMF) at 0° C. under nitrogen, and then by stirring the mixture for 15 min at room temperature. A solution of 3,6-bis(diphenylamino)-9-(4-methoxyphenyl)carbazole (303 mg, 0.5 mmol) in DMF was added to the sodium ethanethiolate solution and heated at 120° C. for 19 hours. After the reaction was stopped by adding several drops of water to the ice cooled solution, 50 ml of water was added, followed by 2N hydrochloric acid until the solution became acidic. The precipitated product was filtered, washed with a large amount of hexane, and dried. The yield of Compound (1), 3,6-bis(diphenylamino)-9-(4-hydroxyphenyl)carbazole, was 250 mg (84.5%). The ¹H-NMR spectrum (300 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ, ppm): 5.50 (s, 1H, OH), 7.00-7.40 (m, 26H, Ar), 7.42-7.59 (m, 2H, Ar), 7.90 (s, 2H, Ar). The ¹³C-NMR spectrum (75.4 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ, ppm): 110.72, 116.55, 118.69, 121.54, 122.57, 123.67, 125.87, 128.53, 128.98, 138.88, 140.24, 148.46, 154.87 (all Ar). The infrared absorption spectrum of the product was characterized by the following the following absorption wavenumbers (KBr windows, in cm⁻¹): 3516 (OH), 3034 (C—H Ar), 1484 (C=C Ar), 1225 (C—O—C).

Compound (2)

A mixture of 3,6-bis(diphenylamino)-9-(4-hydroxyphenyl)carbazole (0.1 g, 0.17 mmol, prepared previously), epichlorohydrin (5 ml), benzyltrimethylammonium chloride (0.02 g, obtained from Aldrich) was refluxed for one hour and the reaction was monitored by thin layer chromatography using an eluant mixture of toluene and hexane in a volume ratio of 4:1. The unreacted epichlorohydrin was removed at reduced pressure under a vacuum to yield an oily material. The oily material was dissolved in dichloromethane, washed several times with water, and dried over magnesium sulphate. The solvent was evaporated under a vacuum generated by a water aspirator and the residue was recrystallized from isopropanol. The product, Compound (2), was purified by column chromatography with an eluant mixture of toluene and hexane in a volume ratio of 4:1. The yield of Compound (2) was 0.065 g (60%). The ¹H-NMR spectrum (300 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ, ppm): 2.79-2.96 (m, 2H, alk.), 3.40-3.42 (m, 2H, OCH₂ oxirane), 3.99-4.35 (m, 3H, OCH₂CH), 6.85-7.24 (m, 26H, Ar), 7.37-7.47 (m, 2H, Ar), 7.75 (s, 2H, Ar). The ¹³C-NMR spectrum (75.4 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ, ppm): 44.86 (OCH₂ oxirane), 50.30 (CH), 69.33 (OCH₂), 110.95, 116.00, 118.92, 121.77, 122.87, 123.97, 126.17, 128.98, 129.27, 139.10, 140.54, 148.76, 158.00 (all Ar). The infrared absorption spectrum of the product was characterized by the following the following

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absorption wavenumbers (KBr windows, in cm^{-1}): 3034 (C—H Ar), 2922, 2853 (C—H Alk), 1484 (C=C Ar), 1225 (C—O—C).

Compound (3)

Compound (3) may be prepared by refluxing Compound (2) with ammonium thiocyanate in tetrahydrofuran for 2-6 hours. The product is isolated and purified by conventional purification techniques such as recrystallization and chromatography.

Compound (4)

Compound 4 may be prepared by the following procedure.

3,6-Diiodo-9-benzoyl-9H-carbazole. Potassium iodate (16.05 g, 75 mmol, available from Aldrich) is added in one portion to a stirred mixture of 9-benzoyl-9H-carbazole (34 mmol, available from Aldrich), potassium iodide (10.96 g, 66 mmol), and acetic acid (100 ml) at 80° C. The reaction mixture is stirred and heated for 1 hour. After the reaction was completed, the acetic acid is removed by distillation. The residue is dissolved in ethyl acetate and washed several times with water and sodium bicarbonate solution. The organic layer is dried over anhydrous magnesium sulfate, filtered, concentrated, and dried. The product is isolated and purified by conventional purification techniques such as recrystallization and chromatography.

3,6-Bis(diphenylamino)-9-benzoyl-9H-carbazole. A mixture of 3,6-diiodo-9-benzoyl-9H-carbazole (5.7 mmol), diphenylamine (1.86 g, 11 mmol, available from Aldrich), powdered potassium carbonate (6.35 g, 46 mmol), copper powder (1.46 g, 23 mmol), and 18-crown-6 (0.4 g, available from Aldrich) is refluxed in o-dichlorobenzene (30 ml) under nitrogen for 24 hours. The copper and inorganic salts are filtered off and the solvent is removed by distillation. The product is recrystallized, washed with methanol, filtered, and dried.

3,6-Bis(diphenylamino)-9H-carbazole. 3,6-Bis(diphenylamino)-9H-carbazole can be prepared by removing the benzoyl group by hydrolysis under either acidic or alkaline condition. The product is isolated and purified by conventional purification techniques such as recrystallization and chromatography.

Compound (4) may be prepared by refluxing a mixture of 3,6-bis(diphenylamino)-9H-carbazole (obtained previously), epichlorohydrin (available from Aldrich), and a catalytic amount of benzyltrimethylammonium chloride (available from Aldrich) in a solvent, such as tetrahydrofuran and ethyl methyl ketone, for 1-8 hours. The reaction may be monitored by thin layer chromatography. After the reaction is completed, the product may be isolated and purified by conventional purification techniques such as recrystallization and chromatography.

Compound (5)

Compound (5) may be prepared according to the procedure for Compound (4) except that carbazole is replaced with 10-benzoyl-N~3~,N~3~,N~7~,N~7~-tetramethyl-10H-phenothiazine-3,7-diamine (N-Benzoyl Leucomethylene Blue, CAS Number 1249-97-4), which may be prepared by the procedure as described in Beil. 27, 398, or be purchased from Chemos GmbH, Regensburg, Germany.

Compound (6)

Compound (2) (3,6-bis(diphenylamino)-9-(4-[2,3-epoxypropyl]phenyl)carbazole, 1 g, 1.54 mmol, prepared previously) and 4,4'-thiobisbenzenethiol (0.19 g, 0.77 mmol obtained from Aldrich) were dissolved in ethyl methyl ketone (15 ml). The reaction was catalyzed by the addition

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of triethylamine (0.5 ml, obtained from Aldrich). After the reaction mixture was stirred at room temperature for 24 hours, the reaction was terminated by pouring the reaction mixture into a large excess of methanol. The product, Compound (6), was precipitated out, filtered and purified by column chromatography using an eluant mixture of hexane and acetone in a volume ratio of 3:2. The yield of Compound (6) was 1.5 g (63%). The ^1H -NMR spectrum (300 MHz) of the product in CDCl_3 was characterized by the following chemical shifts (δ , ppm): 2.71 (m, 2H, CH), 2.67 (s, 2H, OH), 3.30 (m, 4H, SCH_2), 4.16 (s, 4H, OCH_2), 6.85-7.80 (m, 68H, Ar). The ^{13}C -NMR spectrum (75.4 MHz) of the product in CDCl_3 was characterized by the following chemical shifts (δ , ppm): 37.45 (SCH_2), 68.58 (CH), 70.40 (OCH_2), 110.73, 115.74, 118.74, 121.62, 122.71, 123.80, 125.97, 128.42, 128.48, 129.07, 130.34, 131.60, 133.94, 138.90, 140.42, 148.53, 157.53 (all Ar). The infrared absorption spectrum of the product was characterized by the following the following absorption wavenumbers (KBr windows, in cm^{-1}): 3426 (OH), 3034 (C—H Ar), 2923, 2867 (C—H Alk), 1482 (C=C Ar).

Compound (7)

Compound (7) may be prepared according to the procedure for Compound (6) except that 4,4'-thiobisbenzenethiol is replaced with 1,4-benzenedithiol.

Compound (8)

Compound (8) may be prepared according to the procedure for Compound (6) except that 4,4'-thiobisbenzenethiol is replaced with Compound (1). The mole ratio of Compound (1) to Compound (2) is 1:1.

Compound (9)

Compound (9) may be prepared by refluxing a mixture of 3,6-bis(diphenylamino)-9H-carbazole (obtained previously for preparing Compound (4), 1 mole), 1,5-dibromopentane (0.5 mole, available from Aldrich), and a catalytic amount of benzyltrimethylammonium chloride (available from Aldrich) in a solvent, such as tetrahydrofuran and ethyl methyl ketone, for 1-8 hours. The reaction may be monitored by thin layer chromatography. After the reaction is completed, the product may be isolated and purified by conventional purification techniques such as recrystallization and chromatography.

Compound (10)

Compound (10) may be prepared by refluxing a mixture of 3,6-bis(diphenylamino)-9H-carbazole (obtained previously for preparing Compound (4), 1 mole), 3-methyl-3-(bromomethyl)oxetane (1 mole, available from Chemada Fine Chemicals, Israel), and a catalytic amount of benzyltrimethylammonium chloride (available from Aldrich) in a solvent, such as tetrahydrofuran and ethyl methyl ketone, for 1-8 hours. The reaction may be monitored by thin layer chromatography. After the reaction is completed, the product may be isolated and purified by conventional purification techniques such as recrystallization and chromatography.

Compound (11)

Compound (11) may be prepared by refluxing a mixture of 3,6-bis(diphenylamino)-9H-carbazole (1 mole, obtained previously for preparing Compound (4)), 2-chloroethyl vinyl ether (1 mole, available from Aldrich), and a catalytic amount of benzyltrimethylammonium chloride (available from Aldrich) in a solvent, such as tetrahydrofuran and ethyl methyl ketone, for 1-8 hours. The reaction may be monitored by thin layer chromatography. After the reaction is com-

pleted, the product may be isolated and purified by conventional purification techniques such as recrystallization and chromatography.

Compound (12)

Compound (12) may be prepared according to the procedure for Compound (7) except that 4,4'-thiobisbenzenethiol is replaced with 3,6-methylol-9-ethylcarbazole and Compound (2) is replaced with Compound (10). 3,6-Methylol-9-ethylcarbazole may be prepared by reducing 3,6-diformyl-9-ethylcarbazole with a reducing agent such as sodium borohydride and lithium aluminum hydride. 3,6-Diformyl-9-ethylcarbazole was prepared by the following procedure. Dimethylformamide (DMF, 271 ml, 3.5 mol, obtained from Aldrich, Milwaukee, Wis.) was added to a 1-liter 3-neck round-bottomed flask equipped with a mechanical stirrer, a thermometer, and a dropping funnel. The contents were cooled in a salt/ice bath. When the temperature inside the flask reached 0° C., 326 ml of POCl₃ (3.5 mol) was slowly added. During the addition of POCl₃, the temperature inside the flask was not allowed to rise above 5° C. After the addition of POCl₃, the reaction mixture was allowed to warm to room temperature. After the flask warmed to room temperature, 9-ethylcarbazole (93 g, obtained from Aldrich) in 70 ml of DMF was added, and then the flask was heated to 90° C. for 24 hours using a heating mantle. Next, the reaction mixture was cooled to room temperature, and the reaction mixture was added slowly to a cooled 4.5 liter beaker containing a solution comprising 820 g of sodium acetate dissolved in 2 liters of water. The beaker was cooled in an ice bath and stirred for 3 hours. The brownish solid obtained was filtered and washed repeatedly with water, followed by a small amount of ethanol (50 ml). After washing, the resulting product was recrystallized once from toluene using activated charcoal and dried under vacuum in an oven heated at 70° C. for 6 hours to obtain 55 g (46% yield) of N-ethyl-3,6-diformylcarbazole. The ¹H-NMR spectrum (250 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ, ppm): 10.12 (s, 2H); 8.63 (s, 2H); 8.07 (d, 2H); 7.53 (d, 2H); 4.45 (m, 2H); 1.53 (t, 3H).

Example 2

Charge Mobility Measurements

This example describes the measurement of charge mobility and ionization potential for charge transport materials, specifically Compound (1), (2), (6).

Sample 1

A mixture of 0.1 g of Compound (1) and 0.1 g of polycarbonate Z was dissolved in 2 ml of tetrahydrofuran (THF). The solution was coated on a polyester film with a conductive aluminum layer by a trough coating (or "dip roller") method (where the substrate was affixed to a roller that rotated through a trough containing the coating solution). After the coating was dried for 1 hour at 80° C., a clear 10 μm thick layer was formed. The hole mobility value was not reported because the transient time for hole migration through the sample could not be determined due to the very dispersive hole transport nature of the sample.

Sample 2

Sample 2 was prepared and tested similarly as Sample 1, except that Compound (1) was replaced with Compound (2). The hole mobility measurement results are shown in Table 1.

Sample 3

Sample 3 was prepared and measured similarly as Sample 1, except Compound (1) was replaced with Compound (6). The hole mobility measurement results are shown in Table 1.

Mobility Measurements

Each sample was corona charged positively up to a surface potential U and illuminated with 2 ns long nitrogen laser light pulse. The hole mobility μ was determined as described in Kalade et al., "Investigation of charge carrier transfer in electrophotographic layers of chalcogenide glasses," Proceeding IPCS 1994: The Physics and Chemistry of Imaging Systems, Rochester, N.Y., pp. 747-752, incorporated herein by reference. The hole mobility measurement was repeated with appropriate changes to the charging regime to charge the sample to different U values, which corresponded to different electric field strength inside the layer E. This dependence on electric field strength was approximated by the formula

$$\mu = \mu_0 e^{\alpha \sqrt{E}}$$

Here E is electric field strength, μ₀ is the zero field mobility and α is Pool-Frenkel parameter. Table 1 lists the mobility characterizing parameters μ₀ and α values and the mobility value at the 6.4×10⁵ V/cm field strength as determined by these measurements for the four samples.

TABLE 1

Example	μ ₀ (cm ² /V · s)	μ (cm ² /V · s) at 6.4 · 10 ⁵ V/cm	α (cm/V) ^{0.5}	Ionization Potential (eV)
Compound (1)	/	/	/	5.21
Sample 1	—	—	—	/
Compound 2	/	/	/	5.35
Sample 2	4.4 · 10 ⁻⁹	2.2 · 10 ⁻⁷	0.0049	/
Compound 6	/	/	/	5.36
Sample 3	6 · 10 ⁻⁸	2 · 10 ⁻⁶	0.0043	/

Example 3

Ionization Potential Measurements

This example describes the measurement of the ionization potential for the charge transport materials described in Example 1.

To perform the ionization potential measurements, a thin layer of a charge transport material about 0.5 μm thickness was coated from a solution of 2 mg of the charge transport material in 0.2 ml of tetrahydrofuran on a 20 cm² substrate surface. The substrate was an aluminized polyester film coated with a 0.4 μm thick methylcellulose sub-layer.

Ionization potential was measured as described in Grigalavicius et al., "3,6-Di(N-diphenylamino)-9-phenylcarbazole and its methyl-substituted derivative as novel hole-transporting amorphous molecular materials," Synthetic Metals 128 (2002), p. 127-131, incorporated herein by reference. In particular, each sample was illuminated with monochromatic light from the quartz monochromator with a deuterium lamp source. The power of the incident light beam was 2-5·10⁻⁸ W. A negative voltage of -300 V was supplied to the sample substrate. A counter-electrode with the 4.5×15 mm² slit for illumination was placed at 8 mm distance from the sample surface. The counter-electrode was connected to the input of a BK2-16 type electrometer,

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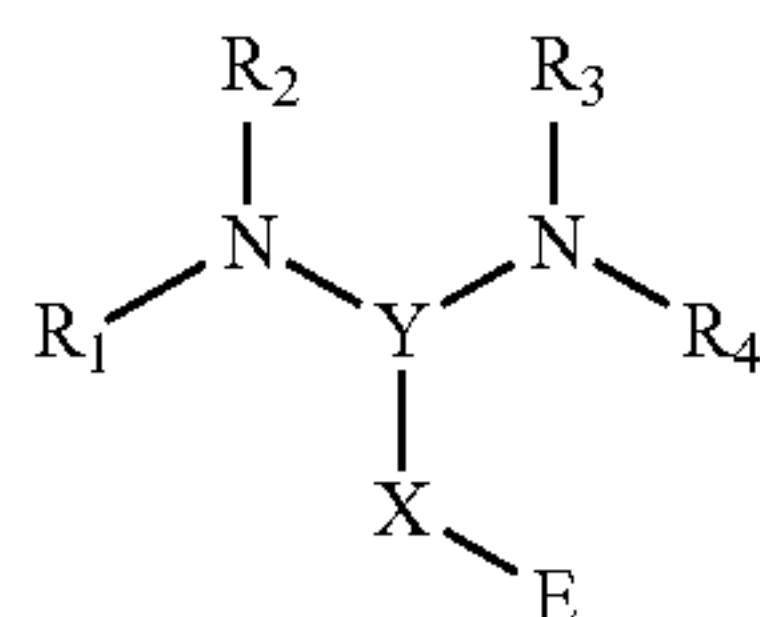
working in the open input regime, for the photocurrent measurement. A 10^{-15} – 10^{-12} amp photocurrent was flowing in the circuit under illumination. The photocurrent, I , was strongly dependent on the incident light photon energy $h\nu$. The $I^{0.5}=f(h\nu)$ dependence was plotted. Usually, the dependence of the square root of photocurrent on incident light quanta energy is well described by linear relationship near the threshold (see references "Ionization Potential of Organic Pigment Film by Atmospheric Photoelectron Emission Analysis," *Electrophotography*, 28, Nr. 4, p. 364 (1989) by E. Miyamoto, Y. Yamaguchi, and M. Yokoyama; and "Photoemission in Solids," Topics in Applied Physics, 26, 1-103 (1978) by M. Cordona and L. Ley, both of which are incorporated herein by reference). The linear part of this dependence was extrapolated to the $h\nu$ axis, and the I_p value was determined as the photon energy at the interception point. The ionization potential measurement has an error of ± 0.03 eV. The ionization potential values are given in Table 1 above.

As understood by those skilled in the art, additional substitution, variation among substituents, and alternative methods of synthesis and use may be practiced within the scope and intent of the present disclosure of the invention. The embodiments above are intended to be illustrative and not limiting. Additional embodiments are within the claims. Although the present invention has been described with reference to particular embodiments, workers skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

What is claimed is:

1. An organophotoreceptor comprising an electrically conductive substrate and a photoconductive element on the electrically conductive substrate, the photoconductive element comprising:

a charge transport material having the formula



where Y comprises an aromatic heterocyclic group;

X is a bond or a linking group;

E comprises a reactive ring group, a reactive functional group, or an ethylenically unsaturated group; and

R_1 , R_2 , R_3 , and R_4 comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group; and

(b) a charge generating compound.

2. An organophotoreceptor according to claim 1 wherein X comprises a $-(CH_2)_n-$ group, where n is an integer between 1 and 20, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group, a BR_g group, or a $P(=O)R_h$ group, where R_a , R_b , R_c , R_d , R_e , R_f , R_g , and R_h are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an acyl group, an alkoxy group, an alkylsulfanyl group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, a part of a ring group,

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or an alkyl group where one or more of the hydrogens of the alkyl group is optionally replaced by an aromatic group, a hydroxyl group, a thiol group, a carboxyl group, an amino group, or a halogen.

3. An organophotoreceptor according to claim 2 wherein X is a methylene group.

4. An organophotoreceptor according to claim 1 wherein Y comprises a carbazolyl group, a phenothiazinyl group, a 5,10-dihydrophenazinyl group, a phenoxazinyl group, an indolyl group, or a pyrrolyl group.

5. An organophotoreceptor according to claim 1 wherein R_1 , R_2 , R_3 , and R_4 comprise, each independently, an alkyl group or an aryl group.

6. An organophotoreceptor according to claim 1 wherein E comprises an epoxy group, a thiiranyl group, an aziridinyl group, an oxetanyl group, a hydroxyl group, a thiol group, an amino group, a carboxyl group, a vinyl ether group, an alkene group, acrylate group, a methacrylate group, an acrylamide group, or a methacrylamide group.

7. An organophotoreceptor according to claim 1 wherein the photoconductive element further comprises a second charge transport material.

8. An organophotoreceptor according to claim 7 wherein the second charge transport material comprises an electron transport compound.

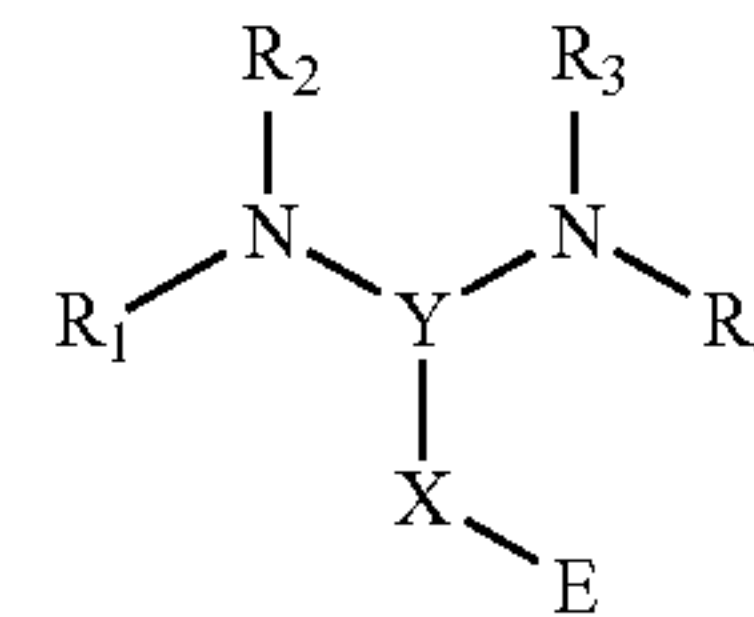
9. An organophotoreceptor according to claim 1 wherein the photoconductive element further comprises a binder.

10. An electrophotographic imaging apparatus comprising:

(a) a light imaging component; and

(b) an organophotoreceptor oriented to receive light from the light imaging component, the organophotoreceptor comprising an electrically conductive substrate and a photoconductive element on the electrically conductive substrate, the photoconductive element comprising:

(i) a charge transport material having the formula



where Y comprises an aromatic heterocyclic group;

X is a bond or a linking group;

E comprises a reactive ring group, a reactive functional group, or an ethylenically unsaturated group; and

R_1 , R_2 , R_3 , and R_4 comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group; and

(ii) a charge generating compound.

11. An electrophotographic imaging apparatus according to claim 10 wherein X comprises a $-(CH_2)_n-$ group, where n is an integer between 1 and 20, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group, a BR_g group, or a $P(=O)R_h$ group, where R_a , R_b , R_c , R_d , R_e , R_f , R_g , and R_h are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an acyl group, an alkoxy group, an alkylsulfanyl group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, a part of a ring

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group, or an alkyl group where one or more of the hydrogens of the alkyl group is optionally replaced by an aromatic group, a hydroxyl group, a thiol group, a carboxyl group, an amino group, or a halogen.

12. An electrophotographic imaging apparatus according to claim 11 wherein X is a methylene group.

13. An electrophotographic imaging apparatus according to claim 10 wherein Y comprises a carbazolyl group, a phenothiazinyl group, a 5,10-dihydrophenazinyl group, a phenoxazinyl group, an indolyl group, or a pyrrolyl group.

14. An electrophotographic imaging apparatus according to claim 10 wherein R_1 , R_2 , R_3 , and R_4 comprise, each independently, an alkyl group or an aryl group.

15. An electrophotographic imaging apparatus according to claim 10 wherein E comprises an epoxy group, a thiiranyl group, an aziridinyl group, an oxetanyl group, a hydroxyl group, a thiol group, an amino group, a carboxyl group, a vinyl ether group, an alkene group, acrylate group, a methacrylate group, an acrylamide group, or a methacrylamide group.

16. An electrophotographic imaging apparatus according to claim 10 wherein the photoconductive element further comprises a second charge transport material.

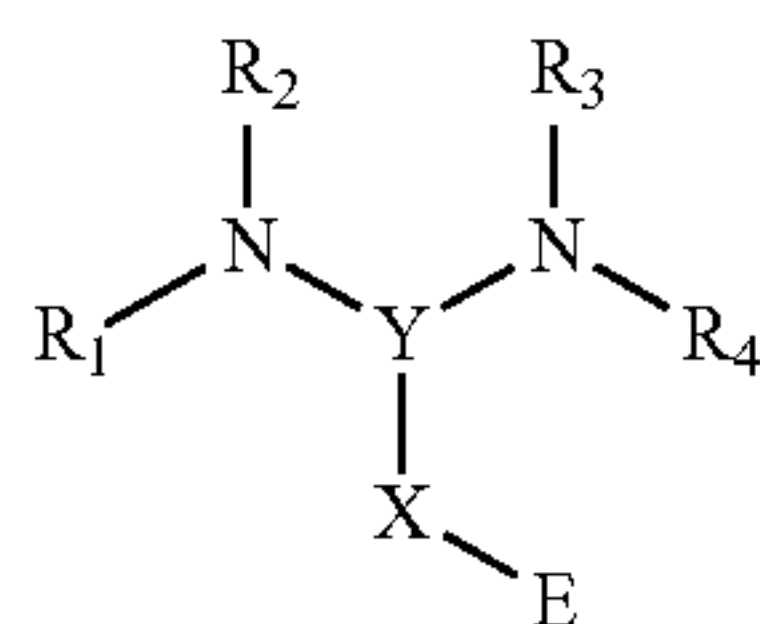
17. An electrophotographic imaging apparatus according to claim 16 wherein second charge transport material comprises an electron transport compound.

18. An electrophotographic imaging apparatus according to claim 10 further comprising a toner dispenser.

19. An electrophotographic imaging process comprising;

(a) applying an electrical charge to a surface of an organophotoreceptor comprising an electrically conductive substrate and a photoconductive element on the electrically conductive substrate, the photoconductive element comprising

(i) a charge transport material having the formula



where Y comprises an aromatic heterocyclic group;

X is a bond or a linking group;

E comprises a reactive ring group, a reactive functional group, or an ethylenically unsaturated group; and

R_1 , R_2 , R_3 , and R_4 comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group; and

(ii) a charge generating compound;

(b) imagewise exposing the surface of the organophotoreceptor to radiation to dissipate charge in selected areas and thereby form a pattern of charged and uncharged areas on the surface;

(c) contacting the surface with a toner to create a toned image; and

(d) transferring the toned image to substrate.

20. An electrophotographic imaging process according to claim 19 wherein X comprises a $-(CH_2)_n-$ group, where n is an integer between 1 and 20, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group,

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a SiR_eR_f group, a BR_g group, or a $P(=O)R_h$ group, where R_a , R_b , R_c , R_d , R_e , R_f , R_g , and R_h are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an acyl group, an alkoxy group, an alkylsulfanyl group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, a part of a ring group, or an alkyl group where one or more of the hydrogens of the alkyl group is optionally replaced by an aromatic group, a hydroxyl group, a thiol group, a carboxyl group, an amino group, or a halogen.

21. An electrophotographic imaging process according to claim 20 wherein X is a methylene group.

22. An electrophotographic imaging process according to claim 19 wherein Y comprises a carbazolyl group, a phenothiazinyl group, a 5,10-dihydrophenazinyl group, a phenoxazinyl group, an indolyl group, or a pyrrolyl group.

23. An electrophotographic imaging process according to claim 19 wherein R_1 , R_2 , R_3 , and R_4 comprise, each independently, an alkyl group or an aryl group.

24. An electrophotographic imaging process according to claim 19 wherein E comprises an epoxy group, a thiiranyl group, an aziridinyl group, an oxetanyl group, a hydroxyl group, a thiol group, an amino group, a carboxyl group, a vinyl ether group, an alkene group, acrylate group, a methacrylate group, an acrylamide group, or a methacrylamide group.

25. An electrophotographic imaging process according to claim 19 wherein the photoconductive element further comprises a second charge transport material.

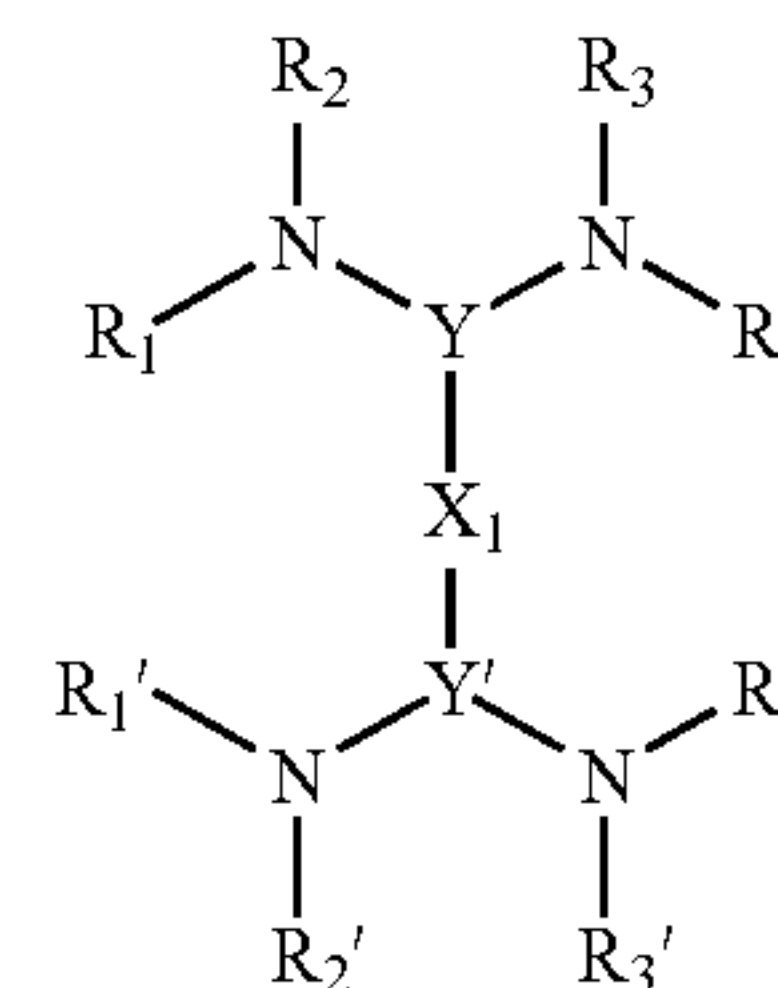
26. An electrophotographic imaging process according to claim 25 wherein the second charge transport material comprises an electron transport compound.

27. An electrophotographic imaging process according to claim 19 wherein the photoconductive element further comprises a binder.

28. An electrophotographic imaging process according to claim 19 wherein the toner comprises colorant particles.

29. An organophotoreceptor comprising an electrically conductive substrate and a photoconductive element on the electrically conductive substrate, the photoconductive element comprising:

(a) a bridged charge transport material having the formula



where Y and Y', each independently, comprise an aromatic heterocyclic group;

X_1 is a first linking group; and

R_1 , R_2 , R_3 , R_4 , R_1' , R_2' , R_3' , and R_4' comprise, each independently, H, an alkyl group, an acyl group, an ether group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group; and

(b) a charge generating compound.

30. An organophotoreceptor according to claim 29 wherein Y and Y', each independently, comprise a carbazolyl

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group, a phenothiazinyl group, a 5,10-dihydrophenazinyl group, a phenoxazinyl group, an indolyl group, or a pyrrolyl group.

31. An organophotoreceptor according to claim 29 wherein R₁, R₂, R₃, R₄, R₁', R₂', R₃', and R₄' comprise, each independently, an alkyl group or an aryl group.

32. An organophotoreceptor according to claim 29 wherein X₁ comprises a —(CH₂)_m— group, where m is an integer between 1 and 66, inclusive, and one of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group,

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a BR_g group, or a P(=O)R_h group, where R_a, R_b, R_c, R_d, R_e, R_f, R_g, and R_h are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an acyl group, an alkoxy group, an alkylsulfanyl group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, a part of a ring group, or an alkyl group where one or more of the hydrogens of the alkyl group is optionally replaced by an aromatic group, a hydroxyl group, a thiol group, a carboxyl group, an amino group, or a halogen.

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